DTU Chemical Engineering
Department of Chemical and Biochemical Engineering

Graduate School Yearbook 2019

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PREFACE

Welcome to this year’s Graduate School Yearbook.

In Denmark, the PhD study is a three-year fulltime programme after graduation with an MSc degree. At DTU Chemical Engineering we host about 100 PhD students from all over the world.

In this book, you can read about most of our current PhD projects. Some students have just initiated their work whereas others are close to writing their thesis. As a new initiative the PhD students have selected the most relevant UN Sustainable Development Goal for their project. This is part of a wider effort at DTU to highlight the importance of technology development to support a sustainable growth in the future. Sustainable growth will require clever solutions - and for that we believe in our young PhD students. They are young and bright and will shape the future development here in Denmark as well as internationally.

The work of our PhD students is of utmost importance to fulfil the mission and vision of our department:

Mission

Being responsible for research, education and innovation, DTU Chemical Engineering will develop and utilize knowledge, methods, technologies and sustainable solutions within:

- Chemical and biochemical process engineering and production.
- Design of chemical and biochemical products and processes.
- Energy and environment.

Vision

DTU Chemical Engineering:

- Is acknowledged as a world leading chemical engineering department.
- Is an attractive partner for university departments and research-based industry.
- Helps to retain, develop and attract knowledge-based national working places.
- Supports development of sustainable solutions in the fields of chemistry, biotechnology, food, pharma and energy through research and research based consultancy.
- Is attractive as a place to work for ambitious and technology-passionate staff members.

We hope you will find the book interesting, and we invite all readers to contact us for further details.

Yours sincerely

Kim Dam-Johansen
Professor, Head of Department

Peter Szabo & Sara Krpović
Editors

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Gas Liberation in Tight Porous Medium

(January 2018- December 2020)

Contribution to the UN Sustainable Development Goals

In spite of the recent progress in renewables, fossil fuels remain the most affordable sources of energy in Denmark and, generally, in the world. Recent studies indicate that Denmark is producing oil in one of the cleanest ways, with the world lowest carbon footprint. A responsible transition to a carbon free economy requires contribution of the petroleum industry until this energy is required for the economy. This work contributes to the responsible, safe, clean and affordable production of the energy.

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Abstract

During oil production, solution gas is liberated and forms a free-gas phase due to the decline in reservoir pressure. The nature of the liberated gas phase is crucial to the reservoir drive mechanism. Within this work, experimental studies of the gas liberation in a porous medium of a low permeability reservoir under decreasing pressure will be conducted. The mobility of the formed gas bubbles and their effect on the effective oil permeability will be determined. Along with the experimental work, the modeling part of the study will be developed to correlate the amount of liberated gas to the reduction of oil permeability.

Introduction

The liberated free-gas phase, generated due to reservoir pressure decline, can either be a handicap or a benefit during oil production. The unfortunate scenario is that disconnected immobile gas bubbles can block individual pore throats, lowering, thus, the effective permeability of the reservoir. Unfavorable pore geometry, along with capillary forces/wettability balance, are the main contributors to that possibility. On the other hand, a favorable case is that the liberated gas bubbles coalesce easily, forming a mobile gas phase, which can provide energy to the reservoir by a competent gas-oil gravity drainage mechanism. For such an effective upwards gas migration, though, crucial parameters are permeability and dip of the reservoir, layering/stratigraphy, as well as the relative permeabilities of the fluid phases[1,2,3].

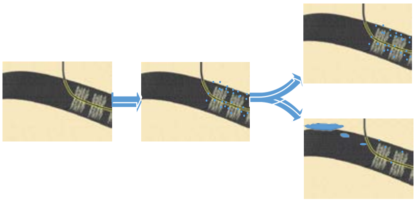

Figure 1: Illustration of the expected fate of the liberated gas bubbles.

Objectives

The experimental study of this work aims to determine the mobility of the formed gas bubbles and their effect on the effective permeability of the oil. The experiments involve gas liberation in a low permeability reservoir sample, induced by pressure decrease. The pressure will range from above to below the saturation pressure, while X-ray computer tomography will be applied to detect the in-situ gas liberation. Effective oil permeability versus pressure drop will be monitored. The onset of gas-phase production, if occurred, will be monitored as well.

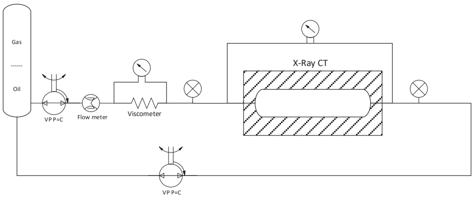

Figure 2: Schematic of the experimental setup.

Along with the experimental work, the modeling part of the study will be developed. For calculating the amount of the produced gas, a previously developed thermodynamic model (DTU) will be adjusted and applied[4]. The model involves oil and gas equilibrium under the action of capillary forces. If the released gas stays in the pores in the form of bubbles, a correlation between the amount of liberated gas and the reduction of oil permeability will be provided. In the case of gas-phase production, a more advanced dynamic model has to be developed for the determination of the gas-oil relative permeabilities.

Results and Discussion

The experiment was conducted on two Stevns Klint's outcrops with approximate porosity and absolute permeability of 42% and 3 mD, respectively. The results show that the liberated gas form disconnected gas bubbles causing the effective permeability of the oil to decrease significantly.

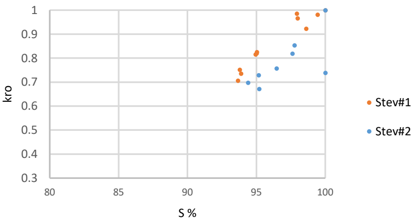

Figure 3: experiment results of Stevns Klint's outcrops

The effect of the liberated gas bubbles on the relative permeability of the oil was modeled based on the theory of effective medium and combinatorial methods developed in statistical physics. The model was then verified using gas-condensate data from the literature[5] then applied to predict the experimental results.

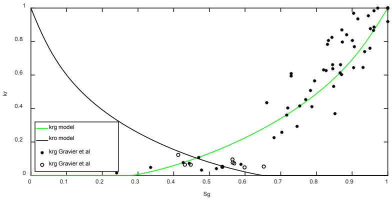

Figure 4: model verification using data from the literature.

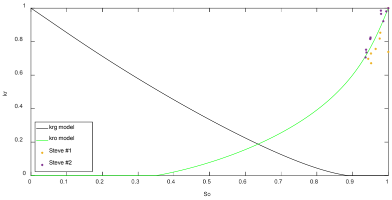

Figure 5: model prediction of the experimental results.

The results show that the model can simulate the effect of liberated gas bubbles on the relative permeability of the oil successfully.

Conclusions

- The liberated gas forms disconnected immobile gas bubbles that block the pore space.
- The reduction of oil relative permeability due to the presence of the gas bubbles is significant.
- A model that predicts the effect of the gas bubbles on effective permeability of the oil is developed and verified.

Acknowledgments

We thank the Danish Hydrocarbon Research and Technology Centre for funding the project and for their close collaboration throughout the project.

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Sustainable process synthesis and design

(May 2017- April 2020)

6 CLEAN WATER AND SANITATION

Contribution to the UN Sustainable Development Goals

Empty reservoirs, dry rivers, thirsty cities. Despite progress, billions of people are still facing water scarcity, lacking access to safe water, sanitation and handwashing facilities. Globally, about 80% of wastewater is returned untreated to rivers, contaminating already depleting freshwater resources. To ensure more sustainable development, and using the state-of-the-art computational technologies, we develop a novel sustainable process design framework that will help engineers to design next-generation wastewater treatment plants.

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Abstract

Mathematical models have become increasingly important tools in developing simulation-based process understanding and assisting decision-making processes in complex engineering systems, among their other uses. Fueled by the continued exponential growth in computing power and the recent boom in available data, these mathematical models have also grown in size and complexity, allowing for the simulation of ever more complex process phenomena at an ever-higher resolution. However, much of what is now possible through these simulation technologies is still not being fully utilized by industrial practitioners, especially in the early stages of engineering design of complex systems, such as wastewater treatment plants. Therefore, this project aims at facilitating the integration of these simulation technologies as well as optimization-based decision making by proposing a new systematic framework enabling design professionals to easily integrate state-of-the-art engineering practices, such as stochastic simulation-based optimization, machine learning assisted global sensitivity analysis, and uncertainty analysis, into the early-stage conceptual design activities. The proposed framework is applied to a case study of wastewater treatment plant design and also implemented in a new decision support tool, SPDLab, which provides a set of tools for wastewater design professionals in a unified framework.

Introduction

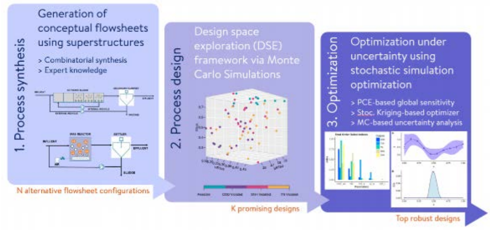
Process systems engineering promotes the application of systematic computer-based approaches to process synthesis and design, which encompasses a vast range of industries and requires integration of a significant amount of knowledge from diverse scientific disciplines, practical industrial experience, and a number of tools and methods to carry out computer-aided process design. One of the critical pain points faced by process design professionals is the lack of available tools regarding the comparative analysis and synthesis of alternative processing networks, hence assisting in implementing innovative processing configurations with newly arising process technologies.

The design problem in wastewater treatment plants, for example, has seen a paradigm shift in recent years in the way of thinking of wastewater, from a waste to treat towards an increasingly valuable source for energy production and resource recovery, which gave rise to the number of available treatment technologies tailored at treatment and recovery of multiple nutrients. Utilities in the developed countries are aiming for energy neutrality or even surplus energy production in their modern wastewater treatment plants (WWTP). The technological advancements in the industry are also driven by the increasingly stringent effluent quality limits, especially on discharged nitrogen and ammonia levels. Given the lack of data regarding these new processes and the uncertainty in the available process data, there exists a need for new supporting methods and tools for both generating alternative processing flowsheets and the selection of the optimum flowsheet under uncertainty. In the following, we proposed a new three-stage framework, which tackles this process design problem in wastewater treatment plants using simulation and optimization-based technologies.

Methodology

At the first stage of the proposed 3-stage-framework, as depicted in Figure 1, superstructures

Figure 1: The 3-stage framework proposed for process synthesis and design.



are employed to represent the technological alternatives space, each of which has its own simulation models, and conceptual design activity is performed by generating alternative process configurations. The second stage explores the design spaces of each process configurations using sampling-based techniques, such as Monte Carlo simulations. These design spaces gather design and operational decisions that would affect the key performance indicators of conceptual flowsheets, among which promising layouts are identified with parallelized simulations. The third and final stage further refines the design spaces by using the global sensitivity analysis techniques on the results of Monte Carlo simulations. This helps to identify key design decisions significantly affecting the design objectives and constraints. Then, the impact of uncertainties on these objectives and constraints is also taken into account using the Monte Carlo method for uncertainty quantification, allowing for informed decision-making. Lastly, an in-house developed simulation-based optimization solver is called to further optimize design decisions, this time allowing for different realizations of uncertainties in the plant influent.

SPDLab: A new decision support tool

In order to assist design professionals involved in early-stage engineering design of next generation wastewater treatment plants, a new decision support tool, SPDLab (standing for sustainable process synthesis and design), has also been developed based on the proposed 3-stage framework [1]. SPDLab provides computational tools for interfacing with complex bioprocess models implemented in Simulink modelling environment and searches for an optimal plant layout configuration for the given design objective and constraints and optimizes design decisions therein using a novel stochastic simulation-based optimization under uncertainty solver. The tool also comes with a model library consisting of a number of high fidelity process models for advanced wastewater treatment technologies, which were developed under the PioneerSTP project [2]. Figure 2 shows the main user interface of SPDLab.

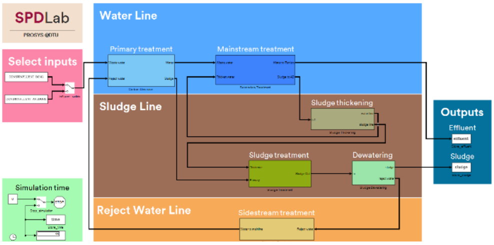


Figure 2: The main user interface of the new decision-support tool, SPDLab, which encompasses several alternative wastewater treatment processes.

Results

The framework was applied to case study of designing energy producing wastewater treatment plant. The tool investigates process configurations with optimal design decisions by providing interactive visualizations. For example, Figure 3 shows feasible populations of designs after effluent quality filters are being imposed. More results from this case study can be found in [1].

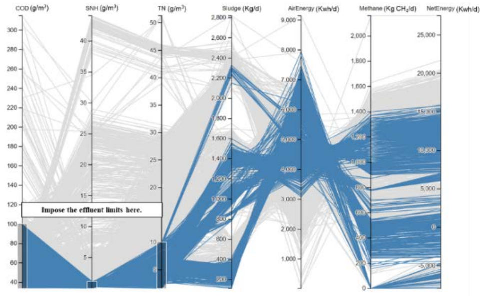


Figure 6: The tool provides interactive visualizations of all feasible designs after imposing regulated effluent quality limits in wastewater treatment plants.

Conclusions

A new simulation optimization-based process synthesis and design framework has been developed and implemented in a decision-support tool. The capabilities of the framework were shown in case studies addressing the design challenges arising in wastewater treatment plants. The results obtained were disseminated through presentations at international conferences as well as dedicated paper contributions to related scientific journals.

Acknowledgements

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Mixed-culture-based syngas fermentation to biofuels

(March 2016- August 2019)

13 CLIMATE ACTION

Contribution to the UN Sustainable Development Goals

The large generation of waste worldwide, the climate crisis and the foreseen future depletion of fossil resources make evident the need to transitioning towards a biobased economy. Biotechnological applications have the potential of tackling all these problems simultaneously though the revalorization of waste and the production of CO_2-neutral commodity chemicals and fuels. This work aims at further developing the syngas fermentation process, which has a great potential for replacing fossil resources by waste recycling, and reducing CO_2 emissions.

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Abstract

In this PhD project, a number of potential tools for improving the control over the metabolism of mixed microbial communities are evaluated in order to enhance their product selectivity using the fermentation of syngas into CH_4 and ethanol as case studies. The tools evaluated include the use of microbial enrichment strategies for selecting specific microbial groups, and the use of thermodynamic principles and modelling tools for rationally designing operational strategies targeting specific bioconversions.

Introduction

The foreseen future depletion of fossil resources and the threat of climate change have motivated a paradigm shift towards the sustainable production of commodity chemicals and biofuels. Microbial production systems have been traditionally based on monocultures. However, over the last two decades, mixed microbial communities (MMC) started to be considered as microbial production biocatalysts owing to the large generation of waste worldwide and the difficulty of treating and revalorizing these waste streams with axenic cultures. Additionally, several unique features of MMC such as non-sterile operation, resistance, resilience and adaptive capacity when facing process disturbances and high long-term functional stability, make them an attractive option for industrial applications [1,2].

The use of MMC is currently expanding beyond the conventional wastewater treatment and anaerobic digestion towards more innovative technological platforms [3]. Syngas fermentation is one of such innovative microbial production platforms, where MMC can be harnessed for the conversion of syngas into a range of chemicals and fuels including CH_4, H_2, carboxylic acids (acetate, butyrate and caproate), and solvents (ethanol, butanol and hexanol) [4,5]. However, the potential of MMC is still limited by their high complexity and the poor understanding of the underlying mechanisms governing their metabolism, resulting in limited process control and generally low product yield and selectivity. Thus, the development of tools integrating the regulation of their metabolic function, population dynamics and microbial interactions and the effects of the operating parameters on the latter is necessary for further advancing MMC-based biotechnological applications.

Objectives

In this PhD project, a range of tools were evaluated in order to address the limited control of MMC-based syngas fermentation processes when targeting the production of ethanol and CH_4. These tools included (i) microbial enrichments for driving shifts in the microbial composition of syngas-converting microbial communities, (ii) the use of thermodynamic principles for the control of the catabolic routes used by MMC, (iii) and modelling tools integrating kinetic and thermodynamic aspects of MMC-based syngas fermentation.

Summary of results

Microbial enrichments

All microbial enrichments carried out were found to drive a significant reduction of the complexity of the MMC, allowing for the selection of specific microbial trophic groups for each case and conditioning the catabolic routes used by the MMC. The enrichment of methanogenic MMC at different incubation temperatures resulted in drastic differences in their community structure and activity rates. While the mesophilic (37˚C) MMC presented a rather complex community structure and low specific CH_4 productivity (1.83±0.27 mmol CH_4/g VSS/h), the thermophilic (60˚C) MMC presented a much simpler metabolic network and much higher specific CH_4 productivity (33.48±0.90 mmol CH_4/g VSS/h). The study of the effect of the pH on the microbial selection and metabolic activity of ethanologenic MMCs resulted in a maximum ethanol yield of 59.15±0.18% of the maximum theoretical when using an initial pH of 5. Changes in the ethanol yield as a function of pH could not be correlated to changes in the microbial composition of each enriched MMC, which indicated that the metabolic shift towards ethanol was strictly driven by the operating conditions.

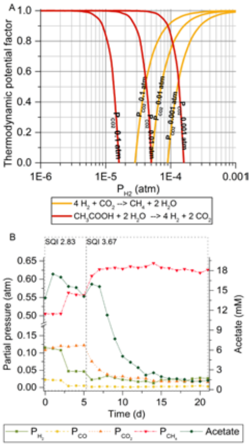

Figure 1: **A** Thermodynamic potential factor of the hydrogenotrophic methanogenesis and syntrophic acetate oxidation as a function of P_{CO2} and P_{H2}. **B** Fermentation profile of mesophilic trickle bed reactor operated in continuous mode.

Thermodynamics-based selection of operating parameters and catabolic route control

The analysis of the interspecies metabolic network of the MMC based on the thermodynamic feasibility of the prevailing reactions during the conversion of syngas allowed for a rational design of operating strategies targeting specific metabolic activities. Using this approach, the aforementioned ethanol yield obtained through pH-based enrichments was enhanced by 22.5% by increasing the initial acetate concentration in the fermentation broth, resulting in a 72.44±2.11% of the maximum theoretical ethanol yield. The reduction of acetate into ethanol using CO was identified as a key reaction to be thermodynamically controlled for enhancing the production of ethanol. Regarding the CH_4 production, the thermodynamic analysis of the methanogenic metabolic network of the MMC used revealed several possible catabolic route control strategies based on the modulation of the partial pressure of CO_2 (P_{CO2}) for enhancing their product selectivity towards CH_4. Experiments carried out in a mesophilic trickle bed reactor under continuous operation confirmed the validity of the catabolic route control strategies, as these allowed increasing the conversion of acetate into CH_4 through syntrophic acetate oxidation by decreasing the P_{CO2} (fig. 1).

Modeling of syngas biomethanation process

The findings related to the methanogenic enrichments, the community structure of the methanogenic MMC and thermodynamic analysis were then implemented in two syngas biomethanation models, which integrated kinetic and thermodynamic considerations for describing the conversion of syngas into CH_4 by MMC. This allowed for an accurate description of the main microbial interactions taking place during the fermentation of syngas, including cross-feeding interactions, mutualistic interactions and mutual exclusion interactions. After parameter estimation, the models could describe the behavior of the mesophilic and thermophilic methanogenic MMC, predicting changes in the catabolic routes used and metabolic shifts within specific microbial trophic groups. Several catabolic route control strategies relying on the modulation of the P_{CO2} and mass transfer were studied based on model simulations.

Conclusions

The findings of this PhD study show that a combination of all tools studied is necessary for achieving an improved control of the metabolic activity of MMCs. This study showed that the use of microbial enrichments and thermodynamic control strategies are essential for the natural selection of desirable microbial trophic groups and the exclusion of the detrimental ones based on either kinetic or thermodynamic competition. On the other hand, the integration of kinetic and thermodynamic aspects into modeling tools is very useful for achieving an accurate design of operational strategies targeting specific biotransformations.

Acknowledgements

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Antimicrobial Polymer Surfaces by SI-ATRP

(January 2017- December 2019)

Contribution to the UN Sustainable Development Goals

Plastic materials used within the medicinal industry such as catheters, stents and implants are generally suffering from bacterial colonization. This can potentially result in severe infections and implant failure posing a great risk for the health of the patient. Treatments are often done with antibiotics, but due to the nature of the infection, development of antibiotic resistant strains are inevitable. This emphasizes the need to develop new superior surface coatings to prevent or reduce hospital acquired infections.

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Abstract

Polymer surfaces are in general prone to attachment of microorganisms, whether it being from marine algae on ships and oil platforms at sea or bacteria and fungi on medical devices. The colonization of implants and medical equipment is a severe health issue in hospital settings and can cause serious infections and implant failure. This project aims to alter the surface chemistry of polymers through grafting of monomers via a controlled radical polymerization method to render the substrates antimicrobial. Controlled polymerization techniques further allow investigation of the structure property relationship of the obtained surface modification in relation to the bactericidal efficiency.

Introduction

Adherence of bacteria to polymeric medical devices is a serious concern as these are capable of causing severe infections and ultimately can be fatal. To accommodate the problem of polymer surface colonization, various compounds and/or techniques have been investigated in an effort to create antimicrobial surface coatings[1,2]. The working principles for these surfaces can, in general, be divided into three categories: 1) repelling 2) leaching and 3) contact killing surfaces. For repelling surfaces, usually a hydrophilic polymer is used to establish a hydration layer, which is capable of protecting the surface against attachment of proteins and bacteria. Leaching surfaces have bactericidal agents incorporated into a given matrix and from here, the agent is able to steadily diffuse and kill surrounding bacteria. Contact killing systems kills bacteria only when in direct contact with the organism. The coupling of peptides and implementation of cationic phosphonium and ammonium groups have been used to create antimicrobial coatings[3]. The bactericidal effect originates from the strong electrostatic interaction with the cell membrane, which is able to disrupt and destabilize it. Contact killing surfaces are of particular interest, since they have antimicrobial properties without release of any active compounds, avoiding the development of resistant bacteria. In this project, an initiator was anchored onto the surface of polymer substrates, in a similar fashion to Fristrup et al. 2012[4], to facilitate surface initiated supplemental activation reducing agent atom transfer radical polymerization (SI-SARA-ATRP) allowing grafting of various monomers, which could then be modified to obtain antimicrobial properties.

Specific Objectives

The objectives of this project is to establish a method that allows for:

- Attachment of an ATRP initiator onto polymer surfaces.
- Grafting of monomers via SI-SARA-ATRP.
- Establishment of an antimicrobial surface able to kill bacteria on contact.

Results and Discussion

To functionalize polymer surfaces, which in general are inert, usually requires activation through the implementation of initiating species or functional groups. Here we apply a simple method of attaching a benzophenone derivatized with an ATRP initiator (Br-BPh), which then permits grafting of monomers through SI-SARA-ATRP (se Figure 1).

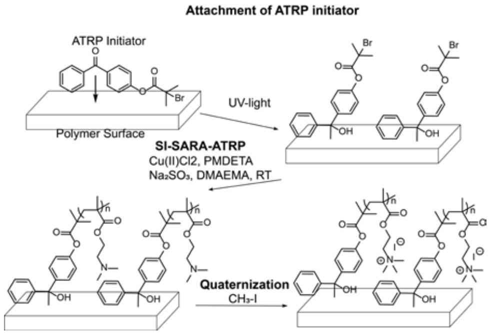
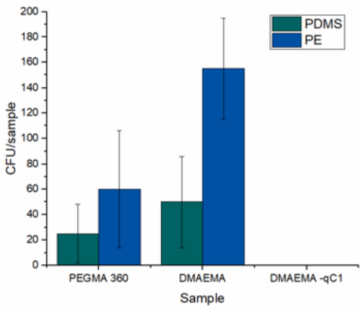


Figure 7: Schematic representation of ATRP initiator attachment followed by grafting of monomer under SI-SARA-ATRP conditions and quarternization of the amine.

By dip coating the polymer with a solution of Br-BPh multiple times, followed by exposure to UV-light, the ATRP initiator is covalently attached to the surface. SI-SARA-ATRP was then conducted at ambient conditions without the use of degassing procedures due to the addition of a reducing agent. It is added in order to protect the reaction mixture, by both reducing the Cu(II) catalyst to the active Cu(I) state but also removes the excess oxygen, preventing unwanted oxidation of the catalyst. The method is generally applicable for grafting of polymer surfaces, and it was used to create surface modifications on both polydimethylsiloxane (PDMS) and polyethylene (PE) using poly(ethylene glycol) methacrylate (PEGMA 360) and 2-(dimethylamino)ethyl methacrylate (DMAEMA). The amine of the surface bound poly(DMAEMA) was subsequently quaternized by iodomethane to yield (DMAEMA-qC1). A modified version of the ISO 22196 test was used to investigate the antimicrobial activity of the substrates against E. coli and the results can be viewed in Figure 2. The graph shows the number of colony forming units (CFU) per sample area, which were 2x1 cm in size.

Figure 8: Number of CFU per sample area after 24 h. exposure to E. coli for PEGMA 360, DMAEMA and DMAEMA-qC1 modified PDMS (green) and PE (blue), n =3, respectively.



Introduction of DMAEMA brushes on the surfaces gave the highest amount of living bacteria attached showing little to no antimicrobial activity. PE substrates were especially prone to adherence of E. coli compared to PDMS. PEG is often used for repellent surfaces and the PEGMA 360 also showed a lower number of bacteria compared to DMAEMA with the PDMS substrate adhering generally lower amounts of bacteria, compared to the PE surfaces. When introducing positive charges through quaternization of the DMAEMA amines no living bacteria was found on the surface for DMAEMA-qC1. The possibly high charge density and strong electrostatic interaction were able to kill all E. coli on both PE and PDMS substrates showing high antimicrobial activity. This shows that surfaces containing quaternary ammonium is highly effective for protection of polymer surfaces against colonization of gram negative E. coli bacteria.

Conclusion

A simple and versatile method to modify various polymer substrates has been tested for PE and PDMS surfaces. The surface modifications proved to have different levels of antimicrobial activity with DMAEMA-qC1 being the most active able to kill 100% of the bacteria on the surface. The substrates will further need to undergo evaluation against other bacterial strains as well as cytotoxic analysis.

Acknowledgements

The project is conducted as a collaboration between Danish Polymer Centre at DTU Chemical and Biochemical Engineering and Coloplast A/S. The work has received funding from both Coloplast A/S and InnovationsFonden.

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Exploring Plasma-Catalysis for Sustainable Production of Chemicals

(October 2018 - September 2021)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Historically, production of chemicals has been made based on fossil resources with a focus to minimize the energy and feedstock consumption leading to large chemical plants. This project will explore the use of a non-thermal plasma in combination with catalysis for a sustainable production of chemicals. The plasma can be powered by renewable energy and act as the reaction enabler instead of high temperature or pressure. This minimizes the use of fossil fuels and further allows a local production also cutting away transport expenses.

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Abstract

An alternative to thermal activation of gas mixtures is the use of a non-thermal plasma. This technology has been shown to convert a mixture of CO_2 and CH_4 into syngas. In this study, a coaxial dielectric barrier discharge reactor with a discharge zone of 10 cm and a gap of 4 mm was used to study dry reforming of methane. A fixed power input of 45 W at a frequency of 3 kHz was used along with ambient pressure and temperature. The influence of different process modes, catalyst only (no electrical energy used), plasma only, and plasma-catalysis were examined. No improved conversion was found when introducing catalytic material in the plasma, which showed a CH_4 and CO_2 conversion of ca. 33% and 22%, respectively. The results indicate that applications of plasma-catalysis should be done with care. Other systems will be studied in the further work.

Introduction

A growing global energy demand and aversion against the use of fossil fuels due to environmental concerns have led to an increased interest in alternative technologies and processes to fossil driven production.

Non-thermal plasma (NTP) processes have been studied for many years in numerous environmental applications [1], especially for air and water pollution control, and in the production of ozone from air [2]. A NTP can be generated by atmospheric pressure discharges, such as corona discharge or dielectric barrier discharge (DBD), by applying a sufficiently strong electric field to the enclosed gas mixture, which then initiates electron avalanches and streamer formation. The electrons are characterised by a much higher temperature than the gas molecules, resulting in a mixture that is in a non-thermodynamic equilibrium [3].

The NTP has been shown to convert a mixture of CO_2 and CH_4 into syngas (see Reaction 1) at atmospheric pressure and near room temperature [4],[5]. The process can be powered by renewable electricity, as the flexibility of the plasma allows for operation that accommodates the fluctuations from such sources. However, a trade-off between the conversion of reactants and energy efficiency has been reported for plasma-based processes [6].

$$\mathrm{CH_4 + CO_2 \rightarrow 2\,CO + 2\,H_2} \qquad 1$$

In this study, the combination of a NTP and catalysis was used to convert CO_2 and CH_4 into syngas under different process modes, i.e. catalyst only (no electrical energy used), plasma only, and plasma-catalysis.

Materials and Methods

A gas mixture consisting of 25 Nml/min CH_4 and 25 Nml/min CO_2 was fed to a coaxial DBD reactor with alumina as the dielectric barrier (reactor wall). A discharge length and gap of 10 cm and 4.5 mm, respectively, were used in this study. The power was supplied by a high voltage amplifier controlled by a function generator. A fixed frequency of 3 kHz and power input of 45 W was utilised for all experiments, along with atmospheric pressure and no addition of thermal heat.

In the plasma-catalysis mode, the plasma zone was fully packed with different types of catalysts: Al_2O_3, 10 wt.% Ag/Al_2O_3, 10 wt.% Cu/Al_2O_3, and 1 wt.% Pt/Al_2O_3.

An online gas chromatograph equipped with a thermal conductivity detector (TCD) and a flame ionisation detector (FID) was used to analyse the product composition. From this, the conversion of the reactants and selectivity of the products were determined.

Results and Discussion

Reaction 1 prescribes a stoichiometric conversion of CO_2 and CH_4. However, a higher CH_4 conversion was observed for the plasma only mode and the plasma-catalyst mode, indicating that other reactions also occur (Fig. 1). The findings correlate with the threshold energies of direct electron-impact dissociation of CO_2 and CH_4, which are 11 and 9 eV, respectively [7]. No improved conversion was found when adding a catalyst in the plasma, which alone achieved a CH_4 and CO_2 conversion of ca. 33% and 22%, respectively. Only the Pt/Al_2O_3 packing showed similar conversion as the plasma only, while Al_2O_3 and Ag/Al_2O_3 showed a lower CH_4 conversion and Cu/Al_2O_3 a lower CO_2 conversion. One reason for the lower conversion is likely a lower residence time of the gas when introducing packing. However, the packing also increases the electrical field in contact points, which here is insufficient to make up for the decrease in residence time.

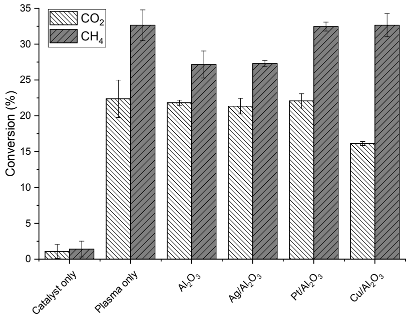

Figure 9: Effect of different operating modes on conversion of the reactants obtained after 5 hours in plasma.

The main products from the dry reforming are CO and H_2 as shown in Fig. 2. Both the Al_2O_3 and Ag/Al_2O_3 packing were observed to enhance the H_2 and CO selectivity slightly compared to the plasma only mode. Interestingly, Al_2O_3 showed the highest H_2 selectivity and loading of an active metal has a negative effect on the selective formation.

Beside CO and H_2, a variety of saturated and unsaturated hydrocarbons were detected in the dry reforming along with oxygenated compounds. The selectivity towards ethane and propane was by far the highest among the by-products with selectivities above 10% for ethane and above 3% for propane.

Remarkably, methanol was found to be formed with the fifth highest selectivity, and for the Cu/Al_2O_3 catalyst, the selectivity reached a value of ca. 3.2%. The relatively high selectivity to ethane indicates dissociation of CH_4 to methyl radicals that recombine to form ethane.

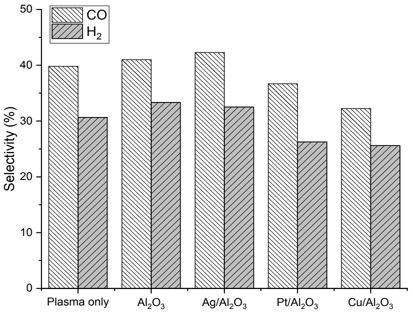

Figure 10: Effect of different catalysts on H_2 and CO selectivity.

Conclusion

It has been shown that the plasma is able to activate the dry reforming feed mixture at ambient conditions. The plasma achieved a conversion of 33% for CH_4 and 22% for CO_2. Addition of a catalyst in the discharge zone led to a lower conversion of the two reactants for most catalysts, except for Pt/Al_2O_3, for which the conversion was similar.

In general, H_2 and CO made up 66 - 77% of the formed products. However, a large variety of saturated and unsaturated hydrocarbons as well as oxygenated compounds was detected in the dry reforming products. Among these ethane, propane, and methanol were formed with the highest selectivity.

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Optimising Plantwide Operations of Biobased Processes

(February 2016 - October 2019)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

In the transition to a circular economy compliant with “Responsible Consumption and Production”, biobased processes are of paramount importance. This concerns energy supply, food production, and not least biobased bulk and fine chemicals. Operating these processes in an optimal way is relevant to this transition. Also healthcare and global aging is a UN recognized priority and Grand Challenge, thus optimal operation of biopharmaceutical plants also falls within this scope.

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Abstract

Biobased processes already constitute an important part of the global, and overproportionally so, of the Danish economy. As biobased chemicals breach into competitive bulk markets, developing countries call for increased amounts of diverse processed foods, and new drug development is sped up, the importance of biobased processes is expected to grow. Due to input- and process uncertainties, entirely unknown states or dynamics, and business cases complicated by small scale, control of bioprocesses is known to be a tough discipline. Plantwide control of bioprocesses has, overall, not received significant academic attention, and this thesis is an attempt at building a better understanding of the chances and challenges. To this end, academic plantwide control literature has been reviewed and is held in contrast to experiences made in actual biobased production sites in Denmark.

Introduction

Plantwide control (PWC) describes a variety of heuristics, methods, and whole frameworks for the optimization of process operation and control in continuous chemical plants. The biobased industry that has traditionally relied on operators and feed-forward- as well as statistical process control to obtain on-spec product, is calling for more efficient processes and broader use of feedback control principles. Advanced process analytical technology, federal regulation with wider design spaces for process optimization purposes, and not lastly increased competition through e.g. rapid development of bioequivalents call for change. This project aims at identifying to which extent PWC principles can be of use in this paradigm shift, and furthermore detect whether there are attributes that characterize PWC of bioprocesses in contrast to PWC of chemical processes.

Biobased Processes

Biobased processes add value to natural feedstocks. Besides types of unit operations, they share a disjoint topology of up- and downstream processes. This is often represented in the according organizational structures as personnel working with one or the other require different expertise [1]. It might also be attributed to some extent to enterprise history and development. It bears the disadvantage that up- and downstream lines do not work properly aligned, and there is, often, a lack of experts with extensive knowledge of and experiences with both.

Plantwide Control

There is a vast amount of academic literature concerned with ‘control of bioprocesses’ – it is important to point out that the discipline ‘plantwide control of biobased processes’ is a fundamentally different one. Where state-of-the-art control of bioprocesses usually deals with monitoring and multivariable optimizing control of upstream processes (bioreactors), see for instance the book by [2], plantwide control - also of bioprocesses - deals with the structural decisions regarding control topology (decentralized vs. centralized) and controller type (PID, cascade control, linear MPC, non-linear MPC, further types of constrained control). The plantwide control task touches many aspects such as operability / operator acceptance, adaptability and maintainability, all of which need to be taken into account to assure that a solution is sustainable and thus long-term optimal.

Academic plantwide control is generally divided into three research streams, namely optimization-based or algorithmic frameworks such as e.g. [3], heuristics, or hybrid frameworks incorporating aspects of the two [4], [5].

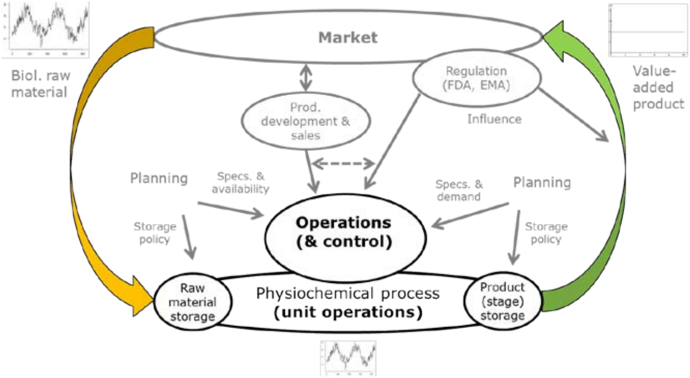

Figure 11: Factors that may directly influence the operational optimality achievable in the process: raw material / process variability, also regulation and planning.

Experiences from Assessing Plantwide Control Structures of two Biobased Production Sites

In the course of the PhD project, two Danish plants (a pectin production- and a pharmaceutical plant) have been visited and observed in great detail with the ambition of assessing the viability of the above-mentioned plantwide control structure synthesis frameworks. In the case of the pectin plant, where the overall operational paradigm is continuous, heuristic plantwide control aspects were found to be applicable and insightful. Through parallelization of batch units (upstream as well as downstream) and the presence of large surge tanks, and not lastly a process that is robust against contamination, continuous operation becomes feasible. However, the absence of a high-fidelity plantwide model is a limiting factor in control structure optimization, the complexity of the task is fortunately reduced by a sequential arrangement of unit operations [6]. At this point, due to unquantified input disturbances, a lack of measurements, and furthermore a disparity between required effort and prospective gains, plantwide modelling of most production sites is unrealistic. This is also true for the assessed pharmaceutical plant, where a further complication arises from the fact that the plant's operational paradigm is batch.

Conclusion

The absence of models of a quality that most researches in PWC would be used to, calls for heuristics. Plantwide control does not account for batch plants, thus PWC of biobased processes should be extended by according methods. Manual operation and a lack of measurements are generally limiting factors, but there is still large optimization potential in the complex, manually operated processes. Relevant actors are depicted in figure 1. In biobased and i.e. pharmaceutical plants, delays in a qualification or audit process are much more costly than a moderate 'waste' of utilities or product. This drastically changes the process design and plantwide control scenario to be considered; future work will aim at collecting and formalizing these differences.

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Characterization of Mixing Performance in Stirred Reactors using Flow Following Sensor Devices

(September 2017 - August 2020)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Contribution to the UN Sustainable Development Goals

Developing new tools that allow the biobased industry to obtain data from production processes which was earlier impossible, will increase the general understanding and effectivenes, making companies producing sustainable solutions more competitive.

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Abstract

Mixing phenomena are regarded as a major factor in unsuccessful scale-up of bioprocesses. Practical constraints related to acquisition of detailed process data leaves behind an extensive knowledge gap in the rough environments of large-scale reactors. With the use of novel flow following sensor devices developed by Freesense ApS, it is now possible to obtain measurements from everywhere inside the reactors, thereby enabling data driven exploration and optimization.

In this study, the sensor devices have been tested in a pilot-scale stirred tank reactor (V_L = 0.6 m3) with two impeller types at different power inputs. Circulation times and spatial distributions were determined based on measurements of hydrostatic pressure by the sensor devices. The determined circulation times were found to be proportional to mixing times determined by tracer experiments. The results have proven the sensor devices as a powerful tool for characterization of mixing during fermentation processes.

Introduction

When scaling up bioprocesses from pilot scale to industrial scale, practical limitations concerning design and monitoring emerges. Even though CFD is considered a useful tool to better understand the effects of scale on bioreactor performance, its practical usefulness is hampered by the lack of full-scale bioreactor data, providing a detailed picture of the real conditions in a tank, and not just at a single point. With technological advances it is now possible to fit multiple sensors into free-floating devices with a reasonable size of Ø45 mm that can gather data on both gradients (pH, temperature, DO) in process parameters and information about the flow characteristics throughout the bioreactors.

One useful flow characteristic that can be determined by the sensor devices is the circulation time. Circulation is proportional to the mixing time and is a useful measure of the degree of mixing in the bioreactor. Literature suggests that the mixing time in a stirred reactor can be approximated by tm ≈ 4tc [1] or by tm ≈ 5tc [2].

Specific objective

Development of a simple method for characterizing mixing performance in large scale and show that the results are in agreement with fundamental research in the area.

Results

Figure 1 shows the axial distributions of the sensor devices at power inputs of 0.02 kW/m^3, 0.11 kW/m^3, 0.21 kW/m^3, 0.31 kW/m^3. The y-axis is normalized to the liquid height (i.e. 0 = bottom and 1 = top) and the x-axis shows the percentage of the total time that the devices spent in each compartment.

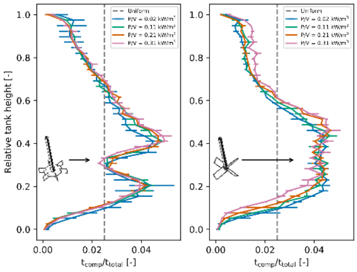

Figure 1: Axial distribution of the sensor devices over the experiment at four levels of power input and

two impeller types. Left: Ruston. Right: Pitched blade.

A comparison between the mean circulation times determined by the sensor devices and experimentally determined mixing times are shown in Figure 2. The circulation and mixing time were determined at the four levels of power input (agitation speed).

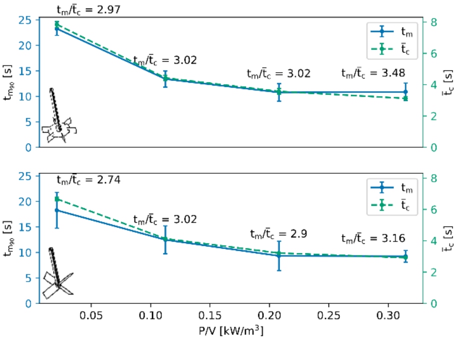

Figure 2: Mean circulation times determined by sensor devices and mixing times determined by traditional tracer experiments. It is evident that the circulation times and mixing times are correlated for both impeller types.

In addition to mean circulation times, the distribution of probable circulation times (CTD) are obtained from the sensor devices. The distributions are shown in Figure 3.

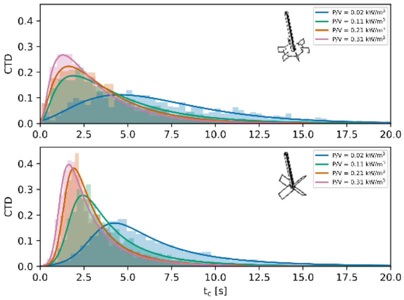

Figure 3: Circulation time distribution (CTD) for four different levels of power input with two impeller types. Top: Rushton. Bottom: Pitched blade.

Discussion

In Figure 1 the devices are not uniformly distributed, but instead more present around the strong circulation paths. This suggests that the devices do not behave as ideal tracers but follow the macroscopic circulation flows. Increased impeller speed does not seem to affect the distribution, which suggests that a more uniform distribution is not related to improved mixing performance. The circulation times in Figure 2 seem to correlate very well with the mixing times determined by tracer experiments. The low standard deviation in the mean circulation times, together with the correlation with the experimental mixing times, suggests that the devices can be used as a reliable method for determination of mixing performance in stirred reactors. In addition, it was possible to determine the CTD (Figure 3), which provides information on the longest expected circulation times. Together with a metabolic regime analysis, this could be utilized to assess potential occurrence cell starvation.

Conclusions

- The sensor devices do not behave as ideal tracers, but follow the macroscopic flow, i.e. circulation flow. The data obtained from the flow-following sensor devices satisfy key characteristics of fully turbulent flow.

- The mean circulation time determined based on measurements of hydrostatic pressure is proportional to traditionally determined mixing time, which implies that the macroscopic flow is sufficient for characterization of mixing performance.

- In addition to a mean value, the distribution of circulation times is obtained. This provides another level of detail, which can be used to assess potential occurrence of cell starvation in a process.

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Operating fermentations with high substrate variability

(January 2017- January 2020)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

Ethanol is a renewable alternative to gasoline as a transportation fuel. However the low costs of gasoline have limited the commercial applications of ethanol. Nowadays, the fast depletion of fossil fuels and the severe environmental consequences of fossil fuels is encouraging governments worldwide to start programs to promote the use of renewable fuels like ethanol. This project aims at optimizing the production of ethanol to increase its commercial competitivity.

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Abstract

The operation of fermentation-based fuel and chemical production processes that utilizes lignocellulosic substrate can be challenging due to the inherent variation in the feedstock. The failure to account for these variations in feedstock results in poor fermentation performance and gives rise to scheduling challenges in both up-stream and down-stream of the fermentation, resulting in overall loss of production efficiency and equipment utilization. This study addresses this practical need by developing a cost-efficient process monitoring solution based on-line spectral data collected with an ATR-MIR spectrophotometer which is used in a novel sequential linear data-driven and a mechanistic model to monitor and predict the consumption of lignocellulose and the production of ethanol in real time.

Introduction

Ethanol has been considered as a renewable alternative to gasoline since the beginning of the 19th century. Since then, the ethanol industry has grown considerably in countries like the United States or Brazil. However, the low process of gasoline limit the commercial competitively of ethanol. In consequence, the growth of ethanol processes have been very supported by government subsidies. In the late eighties, the use of land for ethanol instead of for food raised a strong social opposition to the production of ethanol. This promoted the development of second generation (2G) ethanol processes allowing to produce ethanol from the cellulosic fraction of the agricultural crops. However, 2G ethanol has several challenges that reduce the ethanol productivity and did not become yet a consolidated technology at commercial scale. One of these challenges is the inherent variation in the feedstock, which results in different fermentation profiles. Failing to account for these The failure to account for these variations in feedstock results in poor fermentation performance of the fermentation. In this context, gaining knowledge in real time of the progress of the fermentation is fundamental to adjust the operation to each feedstock, to calculate and predict end-points for fermentations and to take control actions during the fermentation. In this project, a hybrid monitoring approach combining on-line spectral measurements, a linear data-driven model to predict the state variables of the system, and a kinetic model to predict the progress of the fermentation is used to follow and to predict the progress of the fermentation in real time. A scheme of the monitoring approach is shown in the Figure 1.

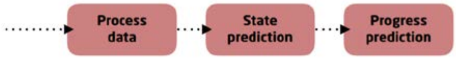

Figure 1: Scheme of the monitoring approach.

Specific Objectives

The objective of this project is to develop and implement a monitoring scheme able to measure the concentration of glucose, xylose and ethanol in real-time and in an automatic manner.

Results

Three different fermentations were ran in batch mode using a 2.5L reactor. The fermentation media, Danish wheat straw hydrolysate, was fermented using *Saccharomyces cerevisiae* and it was monitored every minute using a flow-cell connected to an ATR-MID spectrophotometer (a scheme of the fermentation set-up is shown in Figure 2).

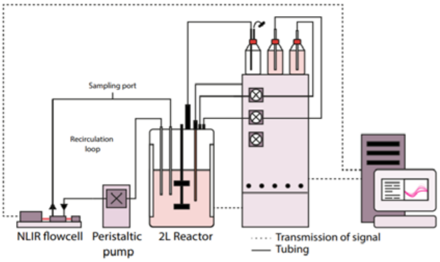

Figure 2. Experimental set-up used for the on-line monitoring approach.

The results of the monitoring approach are shown in Figure 3.

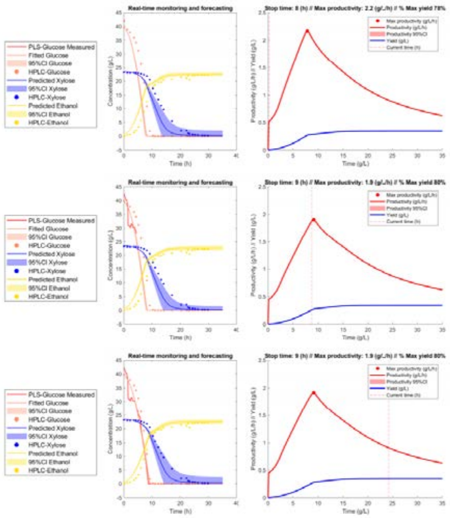

Figure 3. Predictions of the progress of the fermentation.

Discussion

This approach was successfully validated experimentally at lab-scale in three cellulose-to-ethanol fermentations with different initial conditions. The sequential model was updated every 15 minutes allowing re-estimate the state variables and to predict the course of the fermentation in real-time. Glucose and ethanol were successfully predicted with a 95% CI of 1g/L, and xylose was predicted with a 95% CI of 5g/L. In addition to monitoring the progress of the fermentation, it was possible to define end-point criteria for the fermentation based on the predictions made by the mechanistic model.

Conclusions

This method allows to operate the fermentations accounting for substrate variations and opens the opportunity for the implementation of model-based control schemes.

Acknowledgements

This project is supervised by Krist V. Gernaey and Helena Junicke and it is done in close collaboration with Isuru Udugama, Miguel Mauricio Iglesias from the Universidad Santiago de Compostela and Sune Tjalfe Thompsen from the University of Copenhagen. The strain used in this project *S.cerevisiae* CEN.PK.XXX was kindly provided by Professor Carl Johan Franzén, from the Chalmers University of Technology.

List of Publications

1. P. Cabaneros**,** H. Feldmann, M. Mauricio-Iglesias, H. Junicke, J. Huusom, K.V. Gernaey. Biomass and Bioenergy, vol. 127 (2019) 105296

Alternative liquid fuels in burners optimized for low NOX emissions and high burn out

(January 2017- December 2019)

13 CLIMATE ACTION

Contribution to the UN Sustainable Development Goals

The marine and shipping industry contribute significantly to the global human-made emissions of CO_2 and their impact is expected to rise substantially in the future if no action is taken.
Improving the efficiency of the systems used on board of large ships is a first step to help alleviate this issue. Gaining further insight into these systems will also help reduce other pollutants, such as NO_X, and in a future conversion to renewable fuels, which in turn could drastically reduce the CO_2 emissions connected with global trade.

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Abstract

The marine industry is changing with new demands concerning higher energy efficiency, fuel flexibility and lower emissions of NO_X and SO_X. A collaboration between the company Alfa Laval and Technical University of Denmark has been established to support the development of the next generation of marine burners. To this end Computational Fluid Dynamic simulations and experimental methods will be used. During the project, also a novel spray characterization setup has been built and used to observe the changes in atomization quality at different operating conditions and liquid viscosities.

Introduction

On ships of large size, auxiliary boilers are used to meet the steam demand when the heat recovery system of the main engine is not sufficient. Currently, the marine sector is confronting new demands regarding these boilers. It is foreseen that in the next years legislators will demand decreased NO_X, SO_X and particulate emissions in coastal areas. Moreover, ship owners are increasingly interested in fuel flexibility: this would enable them to use the cheaper fuel on the local market instead of running solely on heavy oil fuels. The possibility to use renewable fuels on ships would also help in decreasing their net CO_2 emissions and fuel switching could be done according to the local legislation.

Specific Objectives

The main goals of the project are to support the development of new marine burner able to cope with the above-mentioned demands, providing the partner company with a technology that will help their future global competitiveness, while adding to the current knowledge in the use of renewable energy and providing improved and verified CFD calculations on swirl stabilized flames. The first priority is to evaluate and test the combustion of multiple types of fuels in the boiler and possibly improve its performances with a new burner geometry; the second is to minimize emissions of NO_X, particulates and unburnt hydrocarbons.

CFD Simulations

Experimental and computational methods have been used in the past for simulating both liquid fuel flames and the atomization processes [1] [2] [3]. Results obtained via Computational Fluid Dynamics (CFD) provide detailed information about the local temperatures, compositions and flow fields within the furnace chamber [4]. However, due to its stochastic nature [5] and to the very small length- and time-scales at which it takes place, to simulate the droplet formation process with reasonable accuracy, huge computational resources would be required. To overcome this issue, the spray has not been directly simulated, and the fuel is instead injected into the computational domain as already formed droplets.

The commercial software ANSYS CFX has been used to do 3D CFD simulations of the boiler. During the simulation campaign, several models have been tested for turbulence, radiation and reaction chemistry. Being the CO emissions of interest for the project, the combustion was simulated with a two-step global reaction [6],[7]. Thanks to a sensitivity analysis, the size of the particles used to simulate the fuel spray was singled out as a crucial factor for flame stability and simulation accuracy. No documentation is given from the manufacturers regarding droplet size and velocity distribution, and the range of estimates obtained using correlations found in literature [8] proved to be too broad.

Therefore, a spray characterization setup has been built to observe the atomization quality of the nozzle and gain a better understanding of the atomization process at different operating conditions and for different fluids.

Spray Setup

The spray characterization setup was built to work at the same operating condition of the actual burner. A measuring campaign has been conducted by using water and water-glycerol mixtures, thus reproducing some of the physical characteristics of different fuels [9] [10] for different operating conditions. The spray generated with the setup is then captured with an optical system and the pictures analyzed with a tailor made software to obtain information about droplet size and velocity distributions [11].

Full scale experimental campaign

An experimental campaign on the full-scale boiler was conducted to obtain further insight into the boiler operation and data to validate the CFD simulations.

The campaign included exhaust measurements for gas composition and particulate, and flame mapping for temperature and gas composition. Measurements have been taken for Heavy Fuel Oil and marine diesel, at three different loads, and by varying the excess combustion air between 1% and 6%. The data thus obtained is then used to validate the CFD simulations and to formulate suggested operation conditions for the boiler.

Current Results and Conclusions

Within the CFD simulations a number of different models, parameters and algorithms has been tested. While not universal and limited to the software used, the obtained combination can be considered as a starting point for future modelling. During the CFD study insights in the boiler operation has been obtained: fuel conversion, vortex shedding frequencies and positions of the recirculation zones have been determined. In addition, a sensitivity analysis showed that under the same conditions, a change from 10 to 25 µm of droplet mean diameter, leads to flame lift off.

Using the new spray setup, it was possible to measure droplet size and velocities in different regions of the spray for different operating conditions and fluid viscosity. The data thus obtained has been used to improve the accuracy of the CFD simulations, bringing us one step closer to predict burner performances through computational methods.

Lastly, the measurements gathered during the experimental campaign on the boiler, besides being essential for validating CFD simulations, they also give a comprehensive picture of the emission variations of the boiler within its operating range.

Acknowledgements

The author would like to express his gratitude to the Blue INNOship project and the Chemical Engineering Department of DTU for funding this PhD project

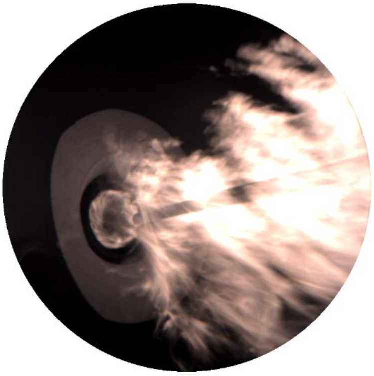

Figure 12: Auxiliary marine boiler flame with suction pyrometer. Frame of video taken during the full-scale experimental campaign.

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Phase behavior of inhomogeneous fluids

(November 2016- April 2020)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Contribution to the UN Sustainable Development Goals

The main goal of this research project is the development of mathematical models suitable to study the behavior of fluids. These models are able to predict thermodynamic properties such as adsorption and interfacial tension. Innovation in this technological area opens new opportunities during the development of complex chemical and biochemical processes that usually require a large quantity of resources in the experimental phase, as mathematical modelling reduces the amount of experiments needed for the design of such processes.

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Abstract

This work focuses in developing a thermodynamic framework for the study of inhomogeneous fluids with classical density functional theory (DFT). With DFT we extend the perturbed chain statistical association fluid theory (PC-SAFT) equation of state to calculate interfacial tension and adsorption of a large range of fluids and its mixtures. DFT offers a unified approach that allows the study of complex systems in a systematic and versatile way in comparison to other approaches, including molecular simulations. We apply our framework to study phenomena related to fluid-fluid and solid-fluid interfaces, like the aforementioned interfacial tension between liquid-liquid and vapor-liquid interfaces, and adsorption of fluids on flat solids. However, the range of applicability of our framework surpasses this set of only two examples. In future projects, we aim to extend the range of our work to include the study of more complex cases of great interest for theory and industry, such as wetting transitions, solvation force, micelle formation, capillary condensation and evaporation, colloidal stability, surfaces with grafted polymers, bio-adhesion, asphaltene adsorption, formation of gas hydrates, among others.

Introduction

The study of fluid-fluid, and solid-fluid interfaces is of great interest for the chemical, biochemical and petroleum industries as it is related to a great number of engineering applications. These applications range from the formation of emulsions and dispersions for food, medicine, detergents, paints and coatings, to improving oil recovery by the addition of surfactants to an oil reservoir, adsorption, wettability, capillarity, confining geometries, etc. [1].

Fluid systems that contain interfaces, like the ones previously mentioned, are classified as inhomogeneous fluids and are studied under the area of surface thermodynamics. The term inhomogeneous comes from the fact that close to the interfaces in the microscopic spectrum, the local density of particles is not uniform due to the effect of such interfaces. The inhomogeneities, or uniformities, give place to specific surface properties that can be studied with classical density functional theory. In Figure 1, there is an example of the behavior of a gas close to a highly attractive wall forming a liquid film. The reduced density profile shown here, represents the ratio between the variable density of the particles with respect to the uniform bulk density. Close to the wall, the reduced density distribution shows layering of particles in the form of oscillations characteristic of adsorbed particles. Further from the wall, the density distribution reaches the bulk gas density. However, in the middle section where the density is higher and liquid-like, there is a transition characteristic of a vapor-liquid interface with its respective interfacial tension.

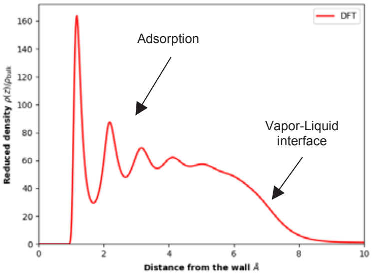

Figure 13: Density distribution of a gas close to a highly attractive wall forming a liquid film calculated with classical density functional theory.

Interfacial tension

Our classical DFT implementation based on the PC-SAFT equation of state inherits the molecular parameters fitted to vapor-liquid equilibrium data, and the binary parameters (kij) used to model the interaction of molecules of different components in a mixture. Examples of interfacial tension of pure components are shown in Figure 2.

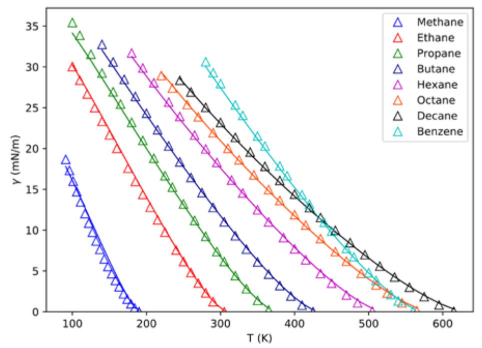

Figure 2: Interfacial tension of pure compounds calculated with DFT [2].

Figure 3 shows an example of how it is possible to improve the correlation of the interfacial tension of a mixture of hexane and ethanol by using DFT to define a better set of parameters for the associating fluid (ethanol).

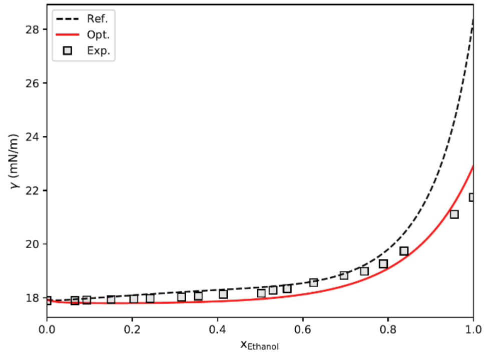

Figure 3: Interfacial tension of mixture hexane-ethanol calculated with DFT with two different parameters for ethanol. Ref. refers to the old set of parameter and Opt. to the optimized parameters.

Adsorption and confined fluids

The study of adsorption is carried out by assuming that the fluids are confined between two attractive walls. This system is described as a confined fluid in a slit-like pore and can be used to study the behavior of fluids in porous media [3]. In the current state of the project, we are able to calculate adsorption in different types of solids and for different types of fluids, accounting for hydrogen bonding and polymers. Examples of adsorption isotherms are shown in Figure 4.

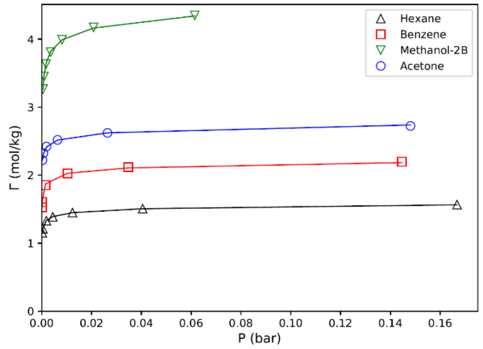

Figure 4: Adsorption of pure compounds calculated with DFT.

Finally, a very important characteristic of fluid behavior in porous media is the shift in the vapor-liquid equilibrium envelope of confined fluids. Figure 5 depicts the effect of the pore size in the phse envelope of water.

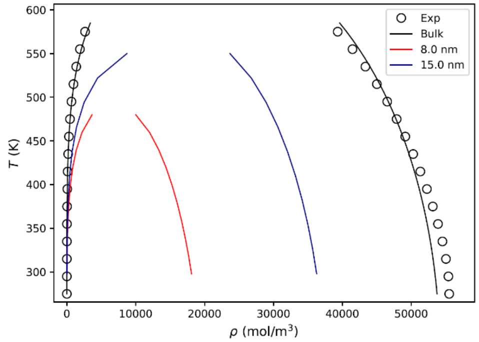

Figure 4: Phase behavior of water in different pore sizes.

Acknowledgements

The Department of Chemical and Biochemical Engineering of DTU for a full PhD-scholarship given to this project.

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Development of a Virtual Educational Bioprocess Plant

(September 2018- August 2021)

4 QUALITY EDUCATION

Contribution to the UN Sustainable Development Goals

To advance into a more sustainable future, we need to facilitate and democratize technical education. The Department of Chemical and Biochemical Engineering of DTU, through my PhD, is developing an open-source software for the teaching of bioprocess. This software can help in the building and to upgrade learning environments for all, through making more affordable and easy technical bioprocesses education. Moreover, we can promote sustainable industrialization (Goal 9) and "doing more and better with less" (Goal 12).

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Abstract
Bioprocesses are experiencing a fast growth with the involvement of complex technologies and therefore, creating an educational need for trainees and new graduates. However, providing an understandable hands-on experience for an increasing number of students and trainees is almost impossible due to time and limitation of resources as well as safety considerations. The combination of educational laboratories and computer simulation could be considered as a match made in heaven as it tackles these issues. Thereby, they are able to support a learning based on action as the users are in control of the decision-making. However, the simulators commonly used in engineering education are not prepared to explain the choices made by the user and consequently, failing in providing a complete educational experience to the unexperienced users. Therefore, in this project, a simulation software that integrates the solution of complex models with a thoughtful learning design and involving motivational elements in envisaged is created.

Introduction

The use of simulators as learning tools in higher education started in the 1970s and many areas such as wastewater treatment [1], robotic [2], electronic circuit [3], control [4], etc. have so far benefited from its use. One of the disciplines that benefits from virtual laboratories is biochemical engineering. Biochemical engineering is based on unit operations across the scales processes, and providing a hands-on experience for the student can be a challenge considering safety and costs. However, mainstream process simulation tools for teaching bioprocess development, design and implementation lack learning design and require previous knowledge of the systems. This is due to the design of commercial simulators commonly aims at solving a specific question and/or develop a process. On the other hand, students require for an instructional computational laboratory to learn something practicing engineers are assumed to already know. That something needs to be defined by carefully designed learning objectives. In addition, the acquisition of knowledge and skills can be facilitated through an enjoyable experience and considering the new habits and interests of the students [5]. Therefore, integrating game elements inside the software platform is one way to tackle this objective.

Specific Objectives

The novelty in this project is within creation of a software tool with the help of a thoughtful learning, real industrial conditions and the consideration of the fast growth in bioprocess. The computational-aided tool is designed according to three milestones:

1) A careful learning design.
2) The use of template models that can be displayed, reused and modified [6].
3) A motivational approach based on gamification.

To do so, it is developed:

- A software architecture (Figure 1). It facilitates a clear structure of the software, with the separation of GUI, the solution of mechanistic models and the database.
- A database to collect and organize the information. The database collects information about the mechanistic models and their parameters, theory of bioprocesses, and a problem-solution database.

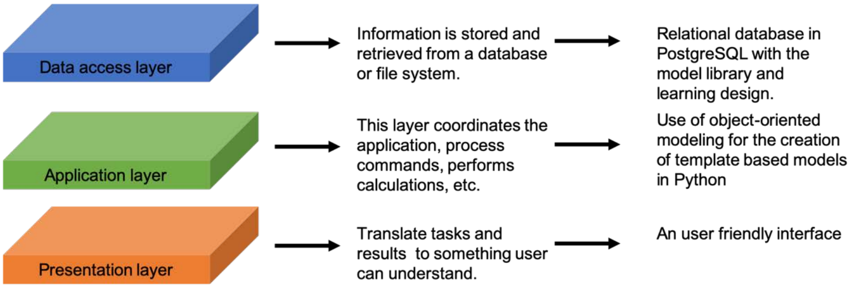

Figure 14. Three-layer software architecture

- A mechanistic models library in which the models are easily explained and it is connected with the implemented models in Python.
- Gamification elements which are integrated in the design of the platform.

Moreover, with the aim to stimulate a collaborative learning, a chatbot will be created to solve questions. The chatbot will have an evil phase in which students will need to develop their critical thinking as not all the solutions of the chatbot will be correct.

Current state of development

The computational tool is the result of the implementation of a previously developed computer-aided modeling framework [8] inside the software architecture (Figure 1).

The software (Figure 2) has been developed to become an interactive webpage.

Figure 15. Initial page of FermProc (domain fermpro01.heroku.com)

The software is written in python programming language as it is *interpreted, interactive, object-oriented*, and it allows the creation of GUI with HTML, CSS and Javascript. As a free object-oriented open-source language, python is suited to create the template model library.

The current platform is preliminary called FermProc and so far, it is focused in the content related to fermentation. Further than a simulator for different bioconversion, FermProc has implemented different mini-games using fermentation concepts, the possibility to modified the different parameters of the chosen models with information related to the parameter theory and range, the creation of a problem-solution database, and multimedia resource.

Conclusions

A bioprocess simulator designed for and by students with a prime pedagogical aim can provide the students and trainees with a tailored tool for the understanding of the complex theoretical knowledge as well as train critical-thinking and decision making abilities inside bioprocess operations.

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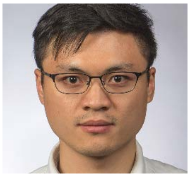
Integrated Ionic Liquid and Process Design

(November 2017- November 2020)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

With growing energy and environmental challenges, novel, sustainable and innovative separation techniques are receiving increasing attention. Because of their non-volatility and other tuneable properties, ionic liquids (ILs) based separation techniques are potential alternatives. In this work, we present an integrated approach, where IL molecular design together with separation process synthesis-design is solved simultaneously. This work could drive the future development of the industry in terms of energy efficient operations.



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Abstract

In the process industries, separation represents a fundamental step to reach the products quality and purity required by the market. Most vapour-liquid based separation techniques involving the separation of close-boiling or azeotropic as well as gaseous mixtures are energy intensive. Downstream separations from bioreactors, on the other hand, are difficult due to relatively small amounts of products in large amounts of reactants and carriers such as water. Ionic liquids (ILs) based separation is being received more attention as a potentially sustainable and energy efficient technology because of their attractive features such as non-volatility, good solubility and selectivity. In this work, a systematic method that combines group contribution (GC)-based property prediction models and UNIFAC models for ILs (UNIFAC-IL) is presented, for use in computer-aided molecular design (CAMD) and process design.

Introduction

As a fundamental step in the process industries, separation processes accounts for 10-15% of the world's energy consumption [1]. Its efficiency could drive the future development of the industry in terms of energy consumption and capital investment. Therefore, intensified separation alternatives are attractive, especially for those involved with energy intensive separation processes. In bio-processes, the downstream separations that contribute a major cost in manufacture are usually difficult because relatively small amounts of products should be recovered from dilute solutions [2]. Therefore, It is advantageous to investigate new technologies that allow energy efficient operation for such energy intensive or difficult separation processes.

Among many emerging separation technologies, the use of ionic liquids (ILs) as solvents is being considered because of their non-volatility and therefore low energy consuming solvent recovery operations [3]. Additionally, unlike organic solvents that may also be classified as volatile organic chemical (VOCs), which would escape into the atmosphere for their high volatilities, ILs exhibit attractive features such as almost negligible vapor pressure, low-melting point, and high thermal and chemical stability. Moreover, ILs have been found to provide good solubility and selectivity, which are important for separation processes. Therefore, ILs provide potential alternatives for the replacement of VOCs in many separation processes. A common IL-based extractive distillation process can be found in Figure 1, where the distillation column is used to separate the light key component (1), from the heavy key component (2), and the entrainer (IL); subsequently, the IL is regenerated by combining a flash drum and an air-operated, atmospheric stripper.

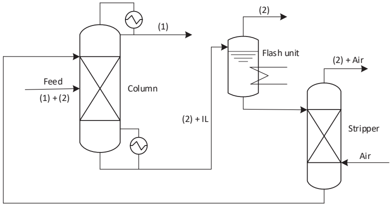

Figure 1: IL-based extractive distillation process

Generally, ILs consist of diverse organic cations which are attached to various substituents and organic or inorganic anions. This results in more than several thousand possible ILs. Finding optimal ILs for specific separation tasks by the usual trial-and-error approach can, therefore, be time consuming and expensive due to the numerous ILs that may be considered as potential solvents. To overcome the limitations of such selection methods, CAILD, a systematic approach that integrates property predictive models and optimization algorithms to reverse engineer molecular structures with unique, is ideally suited. In this way, tailor-made ILs can be generated by adjusting the cations, anions, and substituents. Thus, the "generate and test" approach of generating candidate ILs by tailoring their properties and testing them on the desired separation task is suitable for the design of ILs, as well as for design-verification of their ability to perform specific separation tasks.

Usually, the properties of ILs directly or indirectly impact the performance of the process in which the IL is employed as solvent. However, the classical two-stage design method (molecular design followed by process design) cannot fully represent the strong interdependencies between solvent properties and process performance. Thus, some trade-offs are necessary between tailor-made solvent properties in the design of whole chemical processes. In this work, an integrated approach, where CAILD and separation process synthesis design problems are solved simultaneously, is proposed.

Framework

A framework for integrated IL and process design has been developed, as highlighted in Figure 2. It has five main sections: a) Property model library (GC-based property models, UNIFAC-IL model); b) IL structure (IL-groups set, IL structural parameters, CAILD); c) Process and cost models; d) Integrated IL and process design (MINLP problem formulation and solution); e) Solution and validation (use an appropriate solver and validate the solution through process analysis or experiments (if available).

The work-flow employed by the methodology is as follows: First, retrieve the necessary GC-based property (e.g. density, viscosity, surface tension) models, the regressed UNIFAC-IL model parameters, and the collected group sets (i.e. cations, anions, substituents) from the model library contained in the IL database for the design of IL. Second, formulate the CAILD problem. Third, add the UNIFAC-IL model equations, the GC-based property models, the process and cost models, to formulate the integrated IL and process design problem as a MINLP model. Fourth, solve the MINLP problem with an appropriate solver to obtain, for example, the identified IL, process operating conditions, equipment sizing parameters and associated costs. Fifth, verify the optimal solution through analysis and/or experiment.

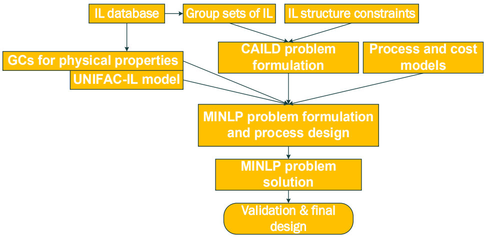

Figure 2: Framework of the integrated ionic liquid and process design

In our previous work [4], a comprehensive database has been established by collecting numerous experimental data of IL properties from different literature sources and also by apriori combinations of new ILs. The database includes 4960 ILs covering 7 cations and 16 anions, out of which around 300 have been synthesized.

Properties of ILs are essential for the design of products and processes containing ILs. In this proposed integrated method, GC-based property models are considered. Because of the molecular structure of ILs, they are also regarded as "designer" solvents, similar rules of CAMD for traditional organic solvent are also introduced to IL design in this work. As well as VOCs, the predictions of solubility and phase equilibria are essential for the design of ILs as solvents in separation processes. In the present work, the UNIFAC-IL thermodynamic model is employed since it can provide desirable prediction results [5].

Conclusion

A systematic method combining GC-based property models, UNIFAC-IL models, CAMD and process design, representing CAILD, to simultaneously determine the optimal IL as a separating agent and the corresponding optimal process design has been developed.

Acknowledgements

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Innovative wound care adhesives with enhanced fluid management

(August 2017- August 2020)

3 GOOD HEALTH AND WELL-BEING

Contribution to the UN Sustainable Development Goals

Chronic wounds often affect and threaten elderly and diabetic patients' life. When not treated effectively, such wounds lead to significant disability, limb amputation and, in the worst-case scenario, increased mortality. Moreover, chronic wounds are a serious burden not only for the patients, but also for the medical system. A single diabetic ulcer has been estimated to cost approximately US$ 50.000 and chronic wounds sums up to nearly US$ 25 billion per year. Therefore, it is important to develop wound care products that effectively promote wound healing.

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Abstract

Skin adhesives with enhanced moisture management are sought-after in medical devices' industry. In this work, an innovative glycerol-silicone adhesive with improved moisture management for medical devices is proposed. The enhancement in fluid handling results from the incorporation of emulsified glycerol. Various parameters are taken into account in order to develop a relevant adhesive, in particular glycerol content, to allow for a controlled moisture absorption.

Introduction

Soft, viscoelastic pressure sensitive adhesives (PSAs) are sought-after in the field of biomedical devices, as they adapt well to human skin [1]. Silicone adhesives are off-stoichiometric silicone elastomers which remain close to the gelation threshold (i.e. with a low crosslinking degree) [1-2]. For medical applications, silicone adhesives are currently the preferred adhesive system due to their gentle skin adhesion properties. These properties are given by the softness and the low surface tension of silicone polymer chains. Nevertheless, silicone adhesives possess poor water transportation due to their hydrophobic nature, and therefore the moisture management provided by silicone adhesives is often insufficient. In addition, as silicone adhesives do not adhere strongly to moist surfaces, the management of perspiration from the user's skin can be challenging and cause the silicone to lose its adhesive properties. This could result in undesired failure of adhesive, which eventually falls off the skin. Furthermore, other dressings, such as hydrocolloid adhesives, usually have higher absorption capacity than silicones, and this renders silicone adhesives less suitable when better fluid management is required. To minimize potential failures, the removal of moisture from the interface between skin and adhesive is crucial to maintain the required adhesion. Failures occur if the amount of fluids released from the skin is larger than the absorption and permeability of the silicone adhesive. Therefore, solutions aimed to improve both these properties are being developed. Current products are manufactured with holes in the silicone layers in order to enhance the moisture transport. However, this not only introduces an additional complicated step in the manufacturing process, but generally provides less flexibility in the product design.

Specific Objectives

Here we present an innovative glycerol-silicone adhesive with enhanced fluid management as a result of emulsified glycerol incorporated evenly throughout the silicone adhesive. Contrarily to the hydrophobic silicone adhesive, glycerol droplets cause water to be absorbed in significant amounts. Thus, glycerol content is evaluated as a tunable parameter that directly affects the moisture management of the hybrid adhesives. It is hypothesized that higher contents of glycerol in the adhesive will lead to higher water absorption and higher water permeability.

Experimental

To create glycerol-silicone adhesives, desired amounts of glycerol and silicone are mixed for 2 min in two steps: 1 min by hand mixing with a spatula and 1 min at 3500 revolutions per minute (rpm) using a dual asymmetric centrifuge SpeedMixer DAC 150 FVZ-K. The obtained glycerol in silicone emulsions were coated with commercial knives to obtain adhesives with thicknesses of around 0.3 mm onto a polyethylene terephthalate (PET) or polyurethane (PU) films. The samples were subsequently cured at 80 °C for 1 h. Samples name were formed using the pattern GX, where G stands for 'glycerol' and X denotes glycerol content as phr (glycerol weight amount per hundred weight parts of silicone rubber) added to the silicone adhesive.

The study of the morphology of cured adhesives was performed using a confocal microscope Leica TCS SP5 X. In the water absorption and permeability experiments, specimens of glycerol-silicone hybrid adhesives of same area and thickness were placed into specific test containers. Subsequently, each container was filled with 20 mL of saline water. The assembled test containers were put in a climatic chamber at 37 °C and 15% RH. The water absorption and permeability were monitored gravimetrically over 24 hours.

Results and Discussion

Glycerol-silicone adhesives were produced by applying high shear forces to the mixtures of glycerol and adhesive premixes. High shear forces caused the glycerol to form discrete droplets distributed evenly within the silicone matrix [4-5]. Confocal microscopy images of cross-sections of cured adhesives with varying content of glycerol are shown in Figure 1. The images elucidate that with increased loading of glycerol the glycerol droplets become larger and more densely distributed.

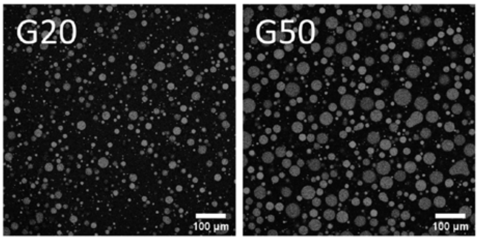

Figure 1: Confocal microscopy images of cured glycerol-silicone adhesives.

Glycerol-silicone composites exhibit an ability to absorb water due to the hygroscopic nature of glycerol [4]. The water absorption is an effect of building up osmotic pressure. In fact, water driven by differences in osmotic pressure in the two different phases fills the glycerol domains embedded in the silicone. Glycerol-silicone adhesives with varying glycerol loadings were tested for their water absorption and permeability and results are presented in Figure 2. As expected, water absorption increased with increasing glycerol content. An overall enhancement of fluid handling capabilities of glycerol-silicone adhesives given by the incorporation of emulsified glycerol was proven.

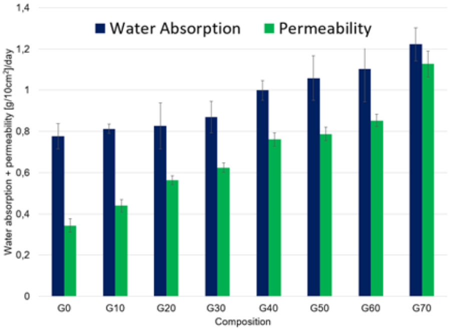

Figure 2: Water absorption and permeability of glycerol-silicone adhesives with different glycerol loadings measured at 37 °C over 24 h.

Conclusion

Glycerol-silicone adhesives are versatile systems, which can be tuned according to the extent of fluids that need to be absorbed. This feature, combined with the gentle skin adhesion properties possessed by silicone, renders glycerol-silicone adhesives potential candidates to be used in medical applications, for instance in the management of chronic wounds.

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CO_2 Capture by Absorption – Experiment and Modeling

(March 2019- March 2022)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Carbon capture, storage, and utilization is a key strategy to help reducing carbon dioxide emissions. While it does not provide a final solution to this problem, it certainly allows for a smoother transition between the current industrial activities towards more sustainable processes. In this project, we investigate a new mixed-salt solvent for the absorption of carbon dioxide from gaseous streams which has the potential to decrease the capture cost and, therefore, make the whole process more economically attractive.

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Abstract

Carbon capture, storage, and utilization is one of the main strategies for reaching the recently established carbon dioxide emission goals. In regard to the capture step, the amine scrubbing process has been widely investigated and is considered therefore one of the most mature technologies for removing carbon dioxide from industrial gases. Nonetheless, the commercial use of such technology is severely hindered by its parasitical power consumption, which greatly affects the cost effectiveness of the whole process. In this project, a new mixed-salt technology for carbon capture is investigated. The new solvent combines mature alternatives for carbon dioxide removal and has presented promising results in laboratory scale tests.

Introduction

Failure to mitigate and adapt to climate change has been ranked recently as the second highest risk to economy, both in likelihood and impact [1]. Consequently, global calls for action have been proposed in recent treatises, such as the Paris Agreement, in order to ensure equitable economic growth while preserving our oceans and forests. Concerning carbon dioxide (CO_2) emissions, carbon capture, storage, and utilization has been highlighted as a strategic technology in different scenarios for reaching our current environmental goals [2].

Amine scrubbing has been used to clean acidic gases for almost 100 years [3]. The process is fairly simple and the absorption unit can be retrofitted to existing plants. These features, combined with the extensive operational knowledge amassed during this period, make this process the leading alternative for CO_2 capture from industrial sources [4]. The technology relies on the reaction between the carbon atom in CO_2 and the amine group to form a C-N bond, which results in the formation of carbamate or bicarbonate species that can be latter reversed by stripping the mixture at high temperatures [5]. In this context, monoethanolamine (MEA) has been the solvent of choice for most demonstrations on carbon capture by absorption since this chemical has a relatively low price and the resulting solvent presents reasonably fast CO_2 absorption rate [6]. Nonetheless, the mixture suffers from poor thermal stability [6] and prohibitive energy consumption for CO_2 stripping and solvent regeneration [7].

A recently developed technology [7] combines two well-known alternatives to amine-based solvents (namely, ammonia and potassium carbonate) to produce a mixed-salt solution which shows promising bench scale results. From an operational perspective, the solvent can capture the majority (> 99%) of the CO_2 fed with high cyclic capacity and it allows the high pressure recovery of CO_2 (up to 40 bar) [8]. The mixed-salt technology also reduces ammonia emissions by favoring the formation of ammonium ion ($NH_4^+{}_{(aq)}$) and seemingly operates without bicarbonate precipitation [8], which would have significant process design implications. Furthermore, preliminary economic evaluations suggest that the new solvent might be less cost intensive than the commercial standards for CO_2 absorption [9].

The next step in the development of the mixed-salt technology is to study possible additives to improve the solvent properties. Among the desired characteristics, the additive should have a low impact in the overall energy consumption, present moderate thermal stability to cope with the stripping temperature and should preferably reduce the ammonia vapor pressure and increase the saturation level of solid species. Finally, the ideal additive should increase either the absorption rate or the loading capacity of the resulting solvent.

Specific objectives

This project focuses on creating a reliable database of relevant properties of a new mixed-salt solvent formulation and on using such results to develop an accurate model that can describe accurately both the absorption and desorption of CO_2 in the new solvent. A new equipment for vapor-liquid equilibrium measurements will be built and solid-liquid equilibrium analysis will be carried out using the existing structure. The ultimate goal is to establish whether the new solvent present significant improvements compared to the initial formulation and to the usual benchmark (MEA-based solvents). This can be done by simulating the process using the developed model to determine the effect of the additive in the (i) process energy consumption, (ii) vapor pressure of ammonia, (iii) bicarbonate solubility, and (iv) CO_2 loading.

Results and Discussion

Initial measurements of the solid-liquid equilibrium of ammonium bicarbonate-amine-water mixtures show that the solubility of ammonium bicarbonate increases as the concentration of amine in the mixture is increased (Fig. 1). These results are in agreement with the theoretical behavior, as the addition of amine increases the pH of the mixture, resulting in a shift in the $NH_4^+{}_{(aq)}$-$NH_{3(aq)}$ chemical equilibrium towards the molecular species (Eq. 1).

$$NH_{3(aq)} + H^+_{(aq)} \leftrightarrow NH_4^+{}_{(aq)} \qquad (1)$$

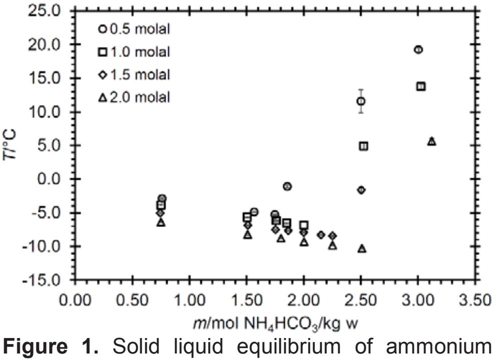

Figure 1. Solid liquid equilibrium of ammonium bicarbonate-amine-water mixtures at 0.5 (○), 1.0 (□), 1.5 (◇), and 2.0 (Δ) molal amine.

While these results show a beneficial aspect of the amine addition, which would seemingly minimize the risk of ammonium bicarbonate precipitation, it also suggests that the concentration of physically dissolved ammonia ($NH_{3(aq)}$) is higher after the addition of amine in the solution. A reasonable prediction for the outcome of this shift is the increase of the ammonia vapor pressure, which could be detrimental for the solvent cyclic capacity and would create additional problems with ammonia slip. This effect will be further investigated after vapor equilibrium measurements are obtained from the equipment under construction.

Conclusions

The mixed-salt technology is a promising alternative for carbon capture by absorption. It is based on off-the-shelf chemicals and can deliver high capture efficiency at a lower cost and energy consumption compared to the standard MEA-based process. This research project focuses on analyzing further improvements for the technology by testing additives that could enhance the characteristics of the solvent.

Acknowledgements

This project is a collaboration between SRI International and the Technical University of Denmark (sub award no PO27088).

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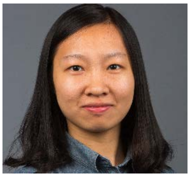
Air-Pollutant Sensor System for Wood Stoves

(September 2017- September 2020)

Contribution to the UN Sustainable Development Goals

Wood stoves are among the most widely used biomass-based distributed energy systems for domestic heating. However, particulate matter (PM) emissions from wood stoves have raised great concerns about indoor and outdoor air pollution. The application of cost-effective control systems to such small-scale combustion units is therefore important for the reduction of PM emissions. In this work, multi-pollutant sensors for the automatic air control system of wood stoves are being developed, which could contribute to a more sustainable future of residential wood combustion.



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Abstract

Small-scale wood combustion units are important renewable domestic heating systems in Europe. However, wood smoke that consists of multiple gaseous and particulate pollutants is harmful to both human health and the environment. In this project, low-cost optical sensors for multi-pollutant monitoring of small-scale combustion units are being developed and tested on a wood stove setup. Good correlations were found between optical sensor signals and emission levels measured by advanced instruments, indicating a promising application of the sensor system to automatically controlled wood-burning stoves.

Introduction

Woody biomass plays an important role in both fossil fuel replacement and climate change mitigation. Moreover, the wood-based system is one of the most cost-effective choices for domestic heating. However, residential wood combustion is also known to be a major source of particulate matter (PM) emissions in Europe [1]. In particular, carbonaceous PM and unburned hydrocarbons emitted from batch wise wood combustion are mainly the products of incomplete combustion. Emission levels of such pollutants are thus closely related to combustion conditions and significantly influenced by firing habits of users [2]. Most importantly, the appropriate air supply along the combustion process is important for the adequate oxidation of combustibles. However, in the case of conventional wood stoves, optimal combustion is hard to achieve with typically manual control of the air supply. Therefore, in order to optimize the combustion conditions and reduce the emissions of the wood stove, a novel sensor-based air control system is being developed in this project. The low-cost optical sensors are expected to be capable of directly measuring multiple pollutants (e.g. soot and tar) in the stove chimney. The on-line signals derived from sensors may be implemented to the air control system for process optimization. With the automatic control system, the influence of inadequate user behavior or maloperations would be reduced.

Specific objectives

- Testing the optical sensor prototype on the wood stove setup and evaluating the performance of the sensor system.
- Investigating the influence of air distributions and fuel-related factors on combustion conditions and emission characteristics of the wood stove.
- Investigating the influential mechanisms of alkali metals on the formation of soot particles

Materials and methods

Combustion tests are performed on a modern wood stove integrated with air staging and an air control system. Key combustion parameters and major air pollutants are measured during the experiments to characterize the combustion conditions and emission profiles of the stove setup, with the main focus on the characterization of PM emissions. More specifically, Scanning Mobility Particle Sizer Spectrometer (SMPS) and Electrical Low Pressure Impactor (ELPI) are used to derive time-resolved PM number/mass concentrations and size distributions with different techniques. The current optical sensor prototype is installed near the inlet of the chimney, consisting of a blue LED sensor at the wavelength of 400 nm and a ultraviolet (UV) LED sensor at the wavelength of 280 nm, as shown in

Figure 1. The measurement principle of optical sensors is mainly based on light absorption, i.e. the absorbance is proportional to the concentration of light absorbing species according to Beer Lambert's law. Such an optical sensor system is expected to be capable of monitoring the emission levels of soot and tar in the flue gas. The performance of the sensors is evaluated by comparing the optical signals with online measuring results derived from the above-mentioned advanced instruments.

Figure 16. The optical sensors installed on the chimney of the wood stove setup

Results and discussion

Figure 1 illustrates the light transmittance measured by optical sensors as well as the PM mass concentrations derived from advanced instruments (with the assumption of uniform particle density) during a typical combustion batch. The decrease in transmitted light signals indicated the presence of light absorbing species (i.e. soot and tar) in the flue gas. Therefore, it can be seen that the optical signals agreed well with the PM concentrations measured by both the SMPS and the ELPI, showing the emission peaks of PM at the initial ignition phase and the late flaming phase of a combustion batch.

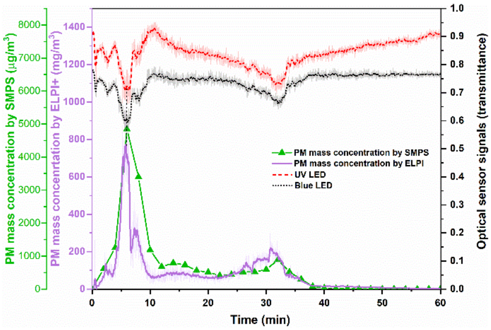

Figure 17. Light transmittance measured by optical sensors and PM mass concentrations derived by advanced instruments

In addition, being interested in the influence of alkali metals on the formation of carbonaceous PM (especially soot), combustion tests with KCl-impregnated wood logs were also performed. The average emission factors of different PM components during one combustion batch are shown in Figure 2. With the addition of around 1 wt% potassium to the wood logs, the average emission factor of soot increased by a factor of 1.3 while that of condensed organic compounds (COC) more than doubled.

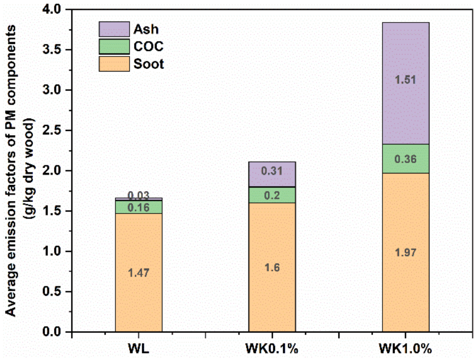

Figure 18. Average emission factors of soot, condensed organic compounds (COC) and ash particles during a combustion batch (WL: normal wood log; WK0.1% and WK1.0%: wood logs impregnated with 0.1% wt and 1.0% wt potassium, respectively)

Conclusions and future work

Testing results of a low-cost multi-pollutant sensor system on a wood stove setup showed good correlations between optical signals with PM emissions measured by advanced instruments. Therefore, the application of the sensor system to automatically controlled wood stoves would be promising with continuous modifications and adaptations. The focus of further improvements is the addition of temperature compensation for the sensors, through which a better baseline of the UV measurement is expected.

Acknowledgements

This PhD project is funded by the Danish EUDP (Energy Technology Development and Demonstration Program) and DTU.

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Polymers for Heavy Duty Coatings

(February 2018 – February 2021)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Contribution to the UN Sustainable Development Goals

Corrosion is a naturally occurring process, which degrades metals. Protection against corrosion is important to consider, especially when constructing large structures such as bridges, oil rigs, and offshore windmills. The economic impact of corrosion across all industries is estimated at 3% of the annual global GDP. A common method of corrosion protection is the use of organic coatings, which protect the metal structure and thus ensure the integrity. This project studies epoxy systems used for anticorrosive coatings.

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Abstract

In this project, epoxy systems used for anticorrosive coatings in harsh environments are investigated by multiple analytical techniques. The physical and chemical properties are characterized to study how paints cure. Two specific examples based on a pure epoxy system and a system with two different amines are used to show how viscoelasticity in the epoxies can be measured and used to characterize their behavior. The results can be used to optimize and develop new paint formulations.

Introduction

Corrosion of steel is greatly accelerated in harsh environments, such as coastal and offshore areas, because aggressive chlorine ions from the saltwater form water-soluble corrosion products, which continuously expose the steel to further corrosion.

Protection of steel structures in harsh corrosive environments is usually done by use of barrier coatings. The purpose of a barrier coating is to form a barrier, which limits the diffusion of corrosive species to the steel surface, thereby preventing the degradation of the steel structure and allowing it to retain its mechanical properties.

Barrier coatings are often based on epoxy chemistry, which is a reaction between molecules containing epoxy and amine functionalities. Epoxy chemistries are used because they are a very robust and versatile set of chemical reactions, which can be tuned to occur at a wide range of temperatures with high efficiency. A variety of different epoxy and amine containing molecules is available for the promotion of desired coating properties. However, epoxy and amine compounds are toxic, and high safety standards are therefore required for the painters using such coatings.

During the course of this project, multiple different epoxy systems are investigated by measuring their chemical reactions during curing, the corresponding change in physical properties as cure progresses, as well as the properties of the fully cured epoxy network.

Specific Objective

The objective of this project is to characterize epoxy systems and use this data to optimize the performance of anticorrosive paints at Hempel.

No single method can fully depict the processes when a paint cures. In order to obtain the full picture, multiple analytical tools are necessary to characterize the epoxy system. The data needed to evaluate the curing and network properties are obtained from viscoelastic tests including Dynamic Mechanical Analysis (DMA) and rheological experiments. The data related to chemical properties are obtained by time resolved Nuclear Magnetic Resonance (NMR), Infrared Spectroscopy (FT-IR) and Dynamical Scanning Calorimetry (DSC), measured at different stages of epoxy curing. In this report, only the DMA and rheology results are presented.

Results and Discussion

In this section, DMA and rheology are applied to characterize the differences in paint curing and network properties of two paints. DMA is commonly used to determine the viscoelastic properties of polymers [1]. Figure 1 shows three graphs, the storage modulus, E' (blue), the loss modulus, E'' (green), and tan(δ) (red) of a DMA measurement. The storage modulus, E', is a measure of the mechanical energy needed to cause deformation of the material. The loss modulus, E'', is the energy which is inelastically dissipated as heat by the material during deformation. Tan(δ) is the ratio between E'' and E'.

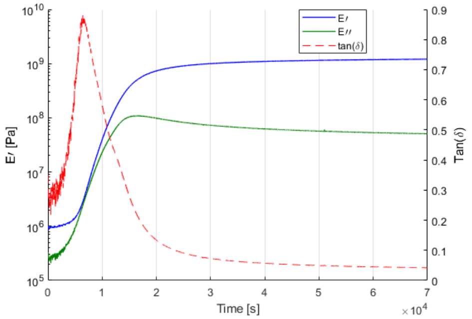

Figure 1: Isothermal dual cantilever DMA curing experiment, performed on an epoxy system.

In the analysis of epoxy curing, E' is used to evaluate the progress of cure and tan(δ) can be used to reveal information about curing mechanisms. The gelation point is the transition of a material from liquid to solid and the appearance of multiple gelation points is an indication of multiple curing mechanisms.

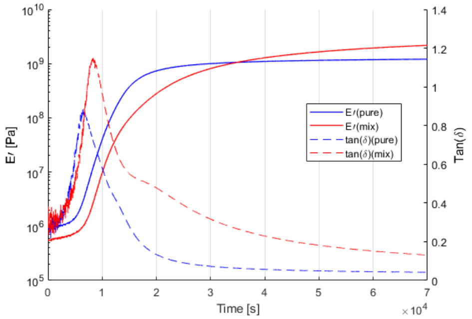

Figure 2: Comparison of two DMA experiments with different compositions. The solid blue curve (pure) is the composition shown on Figure 1, the red curve (mix) is an epoxy with two amine components.

Comparing the solid E' lines in Figure 2, it is observed that the blue system (pure) cures faster than the red system (mix), and the dashed blue line shows a single peak, which indicates that this system reacts with one curing mechanism. The dashed red line reveals a peak and a shoulder, indicating two curing mechanisms, one fast and one slow, and the overall curing speed of the red amine mixture system is therefore reduced. Control of the curing speed is important because of internal stress, which is a detrimental property that can cause cracks and delamination of the coating. Internal stress is often increased with fast curing rates.

Comparing E' of the red and blue curves shown on Figure 2, it is observed that E' of the red curve increases to a higher level over time, and it is therefore clear that the amine mixture has an influence on both the curing rate and the properties of the fully cured network.

This type of measurement can thereby be used to illustrate how different chemical functionalities of curing agents and additives influence the curing mechanisms and physical properties of paints.

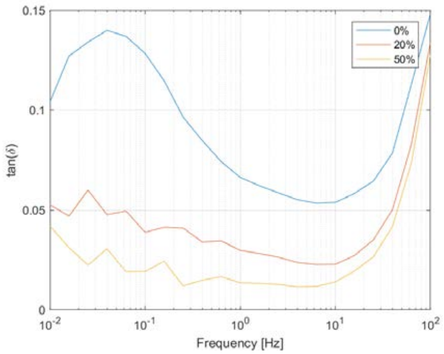

Figure 3: Rheology experiment performed in a dual plate setup, with three epoxy systems, 0% (pure) and two mixtures with increasing amine addition, 20 and 50%.

Figure 3 measures how tan(δ) is related to shear frequency for three compositions with varying amounts of amine mixture. This type of experiment can reveal information about the network structure of cross-linked epoxies after curing, as variation in tan(δ) depends on the molecular dynamics between chains and crosslinks. At low frequencies, tan(δ) is expected to increase because the slow movement enables the polymer to stretch without straining the network. This stress relaxation can be observed on the blue 0% graph, from the increase in tan(δ) between 0.01 and 1 Hz.

Comparing of the three graphs on Figure 3, it can be seen that increasing the amine mixture ratio decreases the low-frequency peak tan(δ), indicating that elastic straining happens at low frequencies. This reduction of tan(δ) for 20% and 50% indicates a more tightly cross-linked network is obtained by increase of amine in the mixed epoxy systems.

Future work

Model epoxy systems and full paint formulations with various additives and curing agents will be tested using mechanical tests and analytical chemistry techniques, in order to determine the physiochemical properties of paints and thereby optimize and develop new paint formulations.

Acknowledgements

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Computer-Aided Product Design of Organic Coatings

(September 2018 - August 2021)

Contribution to the UN Sustainable Development Goals

Developing new tools for product design can lead to innovation and increased effectiveness when formulating products, in this case organic coatings. Predictive methods can be used to substitute unwanted pigments, polymers and volatile organic compounds (VOCs) to reduce hazards and environmental impact during the coating lifespan. Computer-aided product design can drive both growth and innovation by giving the sector access to new technical capabilities in addition to the experience already present.

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Abstract

A combination of databases and models capable of estimating properties will be used to predict functionality in coatings to simplify the extensive process of creating new formulations. These predictions can improve formulation time and accuracy, and substitute unwanted ingredients while maintaining performance, which could be of great interest to an industry that relies heavily on experience. The approach is to create a computational framework by finding the relevant properties for each constituent and to create databases or develop new group-contribution methods depending on available data and project needs.

Introduction

Paints and coatings are complex systems where the final application characteristics and the performance are complex functions of their many ingredients, properties, as well as interactions within the system and with the environment.

Currently, much of the functionality of coatings and paints are determined through experiments and graded on a scale visually. While these tests usually assess the final performance of a complete coating system well enough, they have a very low predictive capability, and formulation therefore depends mostly on experienced formulators and earlier formulations.

The development of a new paint starts with a problem statement. The formulator creates a sample for testing, which is later revised according continues with increasingly small optimization steps as the difference between the paint properties and targeted specifications decrease. Computational aid for a property – performance relationship in coatings can significantly decrease the formulation time and costly experiments by finding a starting point that is closer to the initial specifications, exemplified in figure 1.

Computer-Aided Product Design

Computer-aided product design (CAPD) consists of a combination of computational tools, algorithms, large databases and predictive methods for the estimation of different product properties. The aim is to be able to solve a large range of design problems in coating formulation within a systematic framework that is both flexible and practical [1].

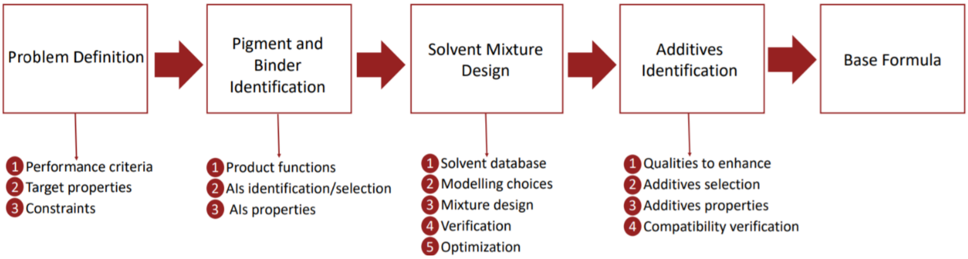

Figure 1. Design scenario of the computer-aided stage for formulation of consumer products such as paints. Pigments and binders are here classified as active ingredients (AIs).

This PhD Project will build upon earlier research by Elise Conte [2] who developed several methods and tools for product-design of consumer-oriented products, including sunscreen, insect repellants, and paints and Spardha Jhamb who focuses on CAPD of solvents and chemical substitution.

As the complex paint systems have to be broken down into its more manageable constituents, the first area of interest for this project is pigments, and later polymers. The continuation of the project will then depend on the obtained results, as well as the outcome of other current research with the final aim of this combined research is an extensive product design framework for a broad range of coatings.

Property Estimations

Depending on the availability of data for each property, as well as the project needs, either databases or new models for property prediction will be used, as it is not feasible to measure the properties of large groups of compounds. For this purpose, group contribution models are preferred due to their high predictive capabilities based on the structural composition of the molecules. The choice of property models is of high importance, as the model strongly affects the reliability of the design, as well as availability of model parameters and uncertainties in the property estimations [3].

Results and Discussion

Application of available group contribution methods for large multi-functional molecules often yields less accurate results, and variations in production and treatment may further complicate any property predictions. Knowing the solubility parameters of both pigments and polymers may be of high importance for any computer-aided design framework, meaning new predictive methods or high-throughput measurements are of interest. The current performance can be seen in figure 2 below.

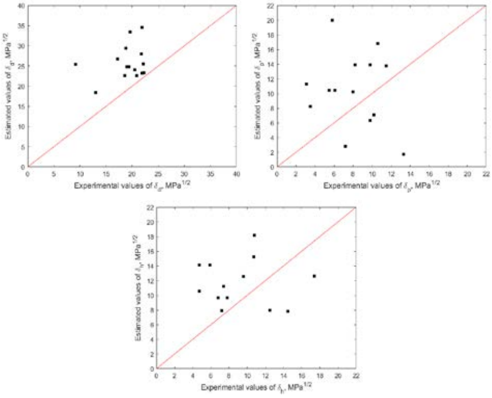

Figure 2. Prediction of Hansen solubility parameters for organic pigments using a second-order group contribution method [4].

While much progress has been made in modern predictive models, many problems must still occur today regarding lack of data and the approximate nature of results. This is why the most common use of computational methods for pigments in the industry today is color matching with the aid of optical properties and spectrometers.

Conclusions and Future Work

The application of CAPD in the paints and coatings industry is still in an early stage and adding new knowledge and tools could be highly beneficial for saving time and resources during trial-and-error experiments. While a number of group contribution methods are already available for certain pigment and polymer properties, additional methods for more accurate results will need to be developed, as well as comparison to measured data currently available.

The full scope of product design extends beyond product problem specifications and product design through modelling and tools, however, further experimental planning and verification is not currently within the reach of this project. Application of the developed framework with property models, databases, methods and tools will instead be tested through a number of case studies that represents relevant problem statements.

Acknowledgements

I would like to extend special thanks the Sino-Danish Center for Education and Research (SDC) as well as the Hempel Foundation Coatings Science and Technology Center (CoaST) for their generous funding and help with this PhD Project.

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Catalytic Deoxygenation of Tars Generated in a Low-Temperature Gasifier for Production of Improved Bio-Fuels

(February 2017- January 2020)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

Thermochemical conversion of biomass has a large potential to improve the share of renewables in the transport sector. In this project, the gasification of wheat straw was investigated with a technology that allows the co-generation of char for soil-amendment and carbon sequestration, bio-fuel for energy storage, and heat and power from the combustible gases. Remote and rural areas and countries without oil resources can highly benefit from this technology by converting locally available biomass. This project investigated how the bio-oil quality can be further improved by catalytic upgrading of the tar vapors.

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Abstract

We investigated the gasification of agricultural residue (wheat straw) in a low temperature circulating fluidized bed (LT-CFB) gasifier, operated specifically in high tar mode in combination with catalytic tar upgrading. This is a flexible process with the potential to co-produce high quality bio-oil, nutrient rich char, and utilize the producer gas for heat and power production. The purpose of this research was to examine the in-line catalytic treatment of the vapors with γ-Al_2O_3 and HZSM-5 zeolites with focus on the change in product distribution and tar quality when conducting the catalytic treatment. With increasing temperature of the LT-CFB pyrolysis chamber, the gas formation was favored at the expense of condensable organics, which separated into an aqueous and oil phase. At a catalyst temperature of 500 °C, the catalytic treatment of the tar vapors effectively improved the bio-oil quality in terms of increased heating value and a reduction in oxygen content, moisture, total acid number, and basic nitrogen content.

Introduction

The reduction of greenhouse gas emissions and the independence of fossil fuels are central and challenging tasks worldwide. The use of biomass instead of fossil fuels for electricity and heat production allows for significant reduction in CO_2 emissions. The low temperature (LT) circulating fluid bed (CFB) gasification process has been developed by the company Ørsted (former Dong Energy) from Denmark in a collaboration with the Technical University of Denmark. The generated tar-rich gas from gasification of alkali rich biomass gas can be combusted in a power plant boiler. The concept has been demonstrated from 100 kW to 6 MW thermal capacity [1], which indicates the applicability of the technology.

Due to the high tar load, gas cleaning is required before the gas can be fed to gas engines or fuel cells. The problem of tar removal from the producer gas can be turned into an opportunity for energy storage into fuels/chemical. For further processing of the bio-oils in conventional oil refineries, a reduction of the bio-oil`s oxygen content and acidity is required [2]. This can be achieved by catalytic vapor treatment prior to tar condensation, thereby creating a system for polygeneration of bio-char, bio-oil, and electricity and heat (Figure 1).

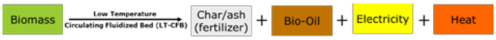

Figure 19: Polygeneration scheme

Specific Objectives

Specifically, this research investigated the catalytic treatment of the tar vapors in order to assess to what extent the fuel properties of the bio-oil can be improved and how the yield of bio-oil is affected. In addition, the effect of pyrolysis temperature on the yield and quality of the tars was investigated.

Results and Discussion

The condensed liquid separated into an aqueous and oil phase, with the latter being the product of interest (=bio-oil). The pyrolysis temperature itself has a strong influence on the tar loading in the producer gas and the properties of the tars (see Figure 2). With an increase in pyrolysis temperature from 570 to 690 °C, the higher heating value of the bio-oil increased from ~30 to 35 MJ/kg due to tar deoxygenation at higher pyrolysis temperatures. However, the yield of tars increased towards lower temperatures (~570 °C) and the energy contribution of tars in the producer gas increased from 16% to 51%. On the other hand, tars collected at higher pyrolysis temperature had improved fuel-properties such as reduced total acid number (TAN) and reduced moisture content (Figure 2).

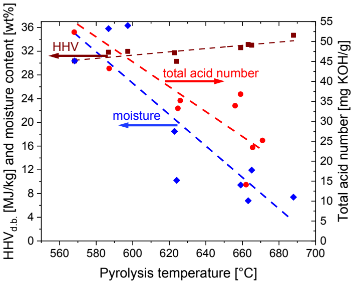

Figure 2: Effect of pyrolysis temperature on the moisture content, higher heating value (HHV), and total acid number in the collected bio-oil fractions.

Table 1 shows the product (carbon) yields with respect to the fed biomass carbon to the LT-CFB. For comparison, the carbon yields obtained with lower pyrolysis temperature (530 °C) at a separate ablative unit [3] are included in Table 1. Note that C_4+ compounds measured in the gas were included in the bio-oil fraction and the yields were normalized to 100%. The char (carbon) yield was 34.8 wt% for the ablative unit, while it was not determined and expected negligible at the LT-CFB due to char gasification.

Table 1: Product yields with respect to the fed biomass carbon and bio-oil properties. Catalyst temperature was 500 °C.

	Abl. Pyrolysis	LT-CFB		
$T_{pyrolysis}$ [°C]	530	~660	~660	~660
Catalyst	-	-	HZSM-5/ γ-Al_2O_3	γ-Al_2O_3
Bio-oil	36.5	21.6	21.0	16.1
Aqueous phase	13.0	4.8	3.4	2.1
Dry gas	15.7	73.7	83.2	74.0
Coke	0	0	4.7	7.8
Bio-oil properties				
TAN [mg KOH/g]	~70	~30	~3	~5
wt% O (d.b.)	~26	~14	~11	~10
Moisture (wt%)	~11	~8	~3	~3

The yield of condensed bio-oil (incl. C_4+ in the gas) was reduced from ~37 to ~22 wt% at the higher pyrolysis temperature of the LT-CFB, but also the carbon lost to the aqueous phase decreased from ~13 to ~5 wt%. The vapor treatment with HZSM-5/γ-Al_2O_3 and γ-Al_2O_3 at 500 °C further decreased the yield of condensed organics. A higher coke yield with Al_2O_3 compared to HZSM-5/γ-Al_2O_3 is attributed to the presence of micropores in the HZSM-5 zeolite and the observation is in line with catalyst testing at the bench scale unit [4]. Both catalysts effectively reduced the acidity and thus the corrosiveness of the bio-oils. In addition, the oxygen content and moisture content of the bio-oils was decreased (Table 1), thereby improving the fuel properties of the bio-oil and its heating value. Due to the confinement effect of the microporous HZSM-5 zeolite, the oils obtained from tar treatment with HZSM-5/γ-Al_2O_3 had increased yield of mono-aromatics such as benzene, toluene and p-xylene.

Conclusions

The in-line catalytic treatment of tars produced from wheat straw in an LT-CFB gasifier showed significant improvement on the quality of the collected bio-oils since the moisture content, oxygen content, TAN and basic nitrogen content decreased while the heating value of the oils was improved. The catalytically treated bio-oils are expected to be better suited for further processing in existing oil refineries. In addition to the catalytic treatment, increased operating temperature of the pyrolysis chamber of the gasifier reduced the tar yield and affected the tar properties. Parallel sampling of tars with or without catalytic treatment was crucial in order to investigate the effect of the catalytic treatment on the tar quality.

Acknowledgements

Funding by the Danish Energy Technology Development and Demonstration Program (EUDP project number 12454) is gratefully acknowledged.

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List of Publications.

1. Eschenbacher *et al.*, Energy & Fuels 33 (1) (2019) 397-412.
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Polyhydroxyalkanoates (PHA) Production from Crude Glycerol

(February 2018- January 2020)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Plastics play a vital role in all sectors of economy. But they are also an increasing concern due to environmental pollution and use of fossil fuels. Bio-based and biodegradable plastics, such as PHA, have the potential to overcome these detrimental impacts. They can be produced from renewable sources, and decomposed in nature. But for these bioplastics to become a reality, their production process also has to be sustainable. The project contributes to the advancement of clean, energy-efficient and economical strategies to produce and purify PHA from organic waste.

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Abstract

PHA (Polyhydroxyalkanoates) are biodegradable and renewable bioplastics produced by bacteria. The objective of the PhD project is to produce PHA from crude glycerol (a by-product of the biodiesel industry) by using mixed microbial consortia (MMC) in order to achieve low PHA production costs. Several culture enrichment strategies have been investigated to increase the substrate conversion and carbon recovery of the process. Membrane bioreactors are currently under investigation to increase the PHA productivity. Moreover, the project has developed a new method for PHA purification based on the use of dilute ammonia. The latter can be reused as a nitrogen source during the PHA production steps, minimizing in this way the wastewater generation and resource use.

Introduction

Fig. 1: PHA film

PHA are a family of polyesters synthesized in bacterial cells as storage polymers in situations of unbalanced growth. Once purified, they present similar properties to polypropylene or polyethylene (Fig. 1). PHA are already in the market, but its presence is very limited, mainly due to their high production costs [1].

The project is based on four strategies to reduce production costs and improve its sustainability:

- The use of crude glycerol (a by-product of the biodiesel industry) as a substrate for PHA production.
- The use of MMC instead of pure bacterial strains for PHA production. MMC do not require sterilization, and are generally more tolerant to inhibitors present in waste substrates.
- The use of cell retention systems, such as membrane bioreactors, to increase the process productivity.
- The development of a sustainable and low-cost purification method.

Crude glycerol can be directly converted to PHA. However, the PHA yield is limited by the side production of glycogen. This phenomenon can be overcome by fermenting the original substrate into volatile fatty acids (VFA), recognized preferred substrates for PHA production. However, the fermentation of glycerol in MMC often leads to the production of 1,3-propanediol (1,3-PDO). This alcohol has already many market applications, but has never been studied as a substrate for PHA production.

In regards to the purification method, PHA are currently purified with expensive and toxic solvents. Most alternatives developed until now lead to significant reduction of molar mass during the recovery and processing of the polymer.

Specific Objectives

- Evaluate 1,3-PDO as a substrate for PHA production, by the application of different MMC enrichment strategies.
- Test the possibility of selective consumption of VFA to PHA, while recovering 1,3-PDO.
- Assess different feeding strategies and bioreactor configurations with cell retention

systems, in order to increase the PHA productivity.
- Investigate ammonia digestion as a method for PHA recovery and purification.

Results and discussion

Classical feast/famine enrichments were performed with nitrogen during the whole enrichment phase. This strategy did not lead to PHA production from 1,3-PDO during the accumulation phase. Changing the enrichment scheme and limiting the nitrogen during the feast phase, PHA production from 1,3-PDO could be attained. Nevertheless, maximum PHA yields from 1,3-PDO were lower than from VFA (0.21 vs 0.74 C_{mol} PHA/C_{mol} Substrate, respectively).

Given that 1,3-PDO is also a high value product, a new enrichment strategy was set in order to avoid the consumption of 1,3-PDO. When the MMC enrichment was performed without 1,3-PDO in the medium, the enriched culture selectively converted VFA into PHA at a very high yield (0.99 C_{mol} PHA/C_{mol} Substrate), while leaving 1,3-PDO in the supernatant (99% recovery) (Fig. 2). At the end of the batch, PHA represented 76 % of the dry weight of the cells.

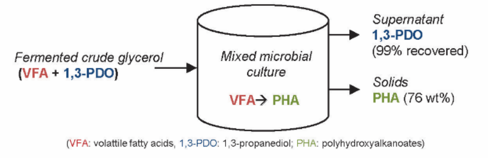

Fig. 2: Selective conversion of volatile fatty acids to PHA with recovery of 1,3-PDO.

In order to increase the productivity of the system and prolong the PHA accumulation, fed-batch strategies were adopted. In fed-batch mode, nitrogen starving cultures got saturated of PHA and could not consume any more substrate. By supplying a limiting amount of nitrogen, bacteria could grow simultaneously to PHA accumulation. This strategy increased 5-fold the PHA productivity.

Membrane bioreactor systems are currently under investigation to increase the productivity even further. These systems allow to replacing part of the fermentation broth without removing cells from the bioreactor. So far, our results have shown that it is possible to operate the membranes without being blocked by the PHA accumulating cells. We have been able to supply 3.5 L of feed to a 0.75 L culture without increasing the reactor volume (Fig. 3), what supposes a volume reduction of more than 80 %.

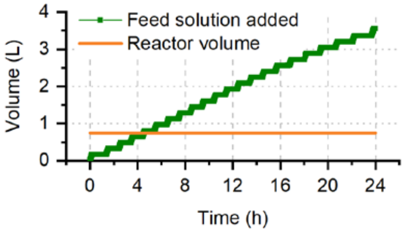

Fig. 3: Membrane bioreactors allow performing fed-batch fermentations with dilute substrates without increasing the reactor volume.

In regards to the PHA purification, ammonia was suggested as a method to digest non-PHA cell material. By using very dilute ammonia concentrations and moderately elevated temperatures, around 90 % PHA purity and recovery were attained. Moreover, the recovered polymers presented high thermal stability during melting at 170 °C, with only 10 % reduction of the molar mass. This value was much lower than with previously suggested methods not employing toxic solvents, which presented over 80 % reduction of the molar mass during melting.

Conclusions

The main conclusions obtained so far within the PhD project are:

- 1,3-propanediol from fermented crude glycerol can be converted to PHA by mixed microbial consortia with a suitable enrichment strategy.
- The overall carbon recovery of the process can be increased by selectively converting VFA in to PHA, while recovering 1,3-PDO.
- Membrane Bioreactors can successfully be applied to fed-batch PHA accumulation to increase the productivity.
- Purification of PHA with dilute aqueous ammonia solutions can lead to high purity and recovery of PHA, while maintaining the thermal stability of the polymer.

Acknowledgements

The authors wish to thank the European Commission (FP7 Grant Agreement no 613667) and DTU Chemical Engineering for the financial support.

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Condensed Phase Chemistry of Inorganic Aerosols from Waste Combustion

(May 2018- May 2021)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Waste management is one of the most important issues for environmental protection. One kind of important waste generated from daily life is municipal solid waste (MSW). Waste-to-Energy (WtE) is considered as a mature technology to convert MSW to heat and/or power. However, WtE technology is challenged by incinerator / combustor corrosion. We are focusing the understanding condensed phase chemistry of inorganic aerosols generated from waste combustion. Furthermore, develop and validate of models to describe the condensed phase chemistry.

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Abstract

Waste-to-Energy (WtE) technology is a way to recover the energy from municipal solid waste (MSW) incineration into reusable heat and/or electricity. However, it faces a huge corrosion problem caused by inorganic aerosol condensation at ~400°C in the incineration chamber and superheaters. This PhD project focus on the condensed phase chemistry of its modeling in a systematically way.

Introduction

Waste management is one of the most important issue for environment protection. It is reported that approximately 212.22 Mt (9%) of municipal solid waste (MSW) generated in 2016. This number (in **Figure 2**) is expected to be 246 Mt in 2035[2]. Furthermore, the amount of residual (not-recycled) waste will be increased to 142 Mt. Current Waste-to-Energy capacity is 90 Mt and the capacity for co-incineration is around 11 Mt [2]. This leaves around 40 Mt gap. Hence, waste management of MSW is facing a big challenge and it demands a high efficiency and affordable waste treatment method in order to maintain a reasonable level of community hygiene. One of the most frequently used technology is called Waste-to-Energy (WtE). It is a way to recover the energy from waste matter into reusable heat and/or electricity [3]. Even though a variety of waste conversion processes available, grate firing is used as a dominant WtE technology, because of its simplicity and relatively low capital cost.

Figure 1 is a schematic of incineration system. The waste was feed gradually into the incinerator and combusted in the chamber. Heat from the burning waste is used in heat recovery units and steam from this is piped to a turbine generator to create electricity. Flue gases containing fine ash then pass through an air pollution control system to treat acid pollutants such as SO_2 and also dioxins. The gases then pass through a fine particulate removal system and are released through the chimney stack.

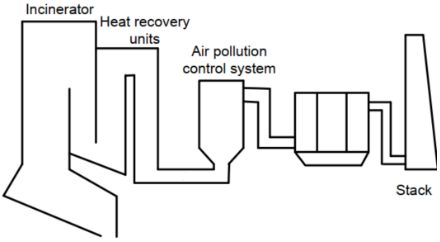

Figure 20 Schematic of a moving grate incinerator.[1]

Challenges WtE incineration are facing:

The main concern pollutants found in the ash left in the incinerator and emitted from the chimney are dioxins, acid gases, nitrogen oxide, heavy metals and particulates. Besides these, incinerator/combustor corrosion is another challenge. Municipal waste contains various constituents and impurities that induce corrosion attacks on boiler tubing. Among the leading contributors are chlorine, sulfur, zinc, lead, sodium and potassium. During combustion, various metallic chlorides and sulfates as well as HCl and SO_2 in flue gas are formed and then deposited on the cooler surfaces, such as the water wall and superheater tubes, and scrubber surface [2,3]. Due to the low melting points and high vapor pressures of many metallic compounds, severe corrosion will occur when carbon and low alloy steels are in contact with these salts in its condensed phase.

Up to date, the condense phase chemistry of heavy metal such as sulfation, chlorination reaction and chemical interaction with alkali species are lack of systematically investigation. Only KCl sulfation reaction has been investigated by experiment and modeling[4,5] as well as sulfur species additives (e.g. ammonium sulfate, ferric sulfate etc.) sulfation reactions[6]. Furthermore, the influences of the condensed phase chemistry on superheater corrosion is still unclear.

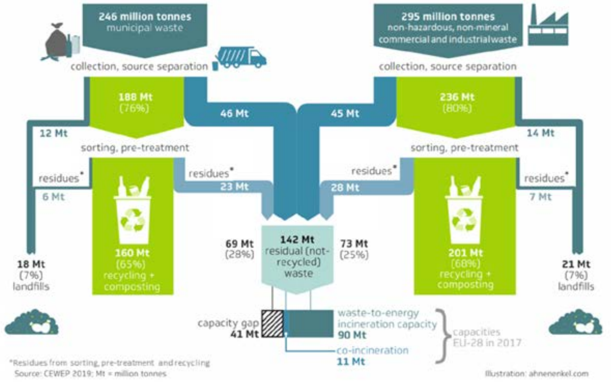

Figure 21 Circular Economy Package-Ambitious Targets for 2035[7]

Specific objectives

The overall objective is to achieve an improved understanding of the condensed phase chemistry of inorganic aerosols generated from waste combustion, including:

- Condensed phase sulfation and chlorination of heavy metal aerosols;
- Interactions of heavy metal aerosols and alkali aerosols in the condensed phase chemistry;
- Influences of the condensed phase chemistry on superheater corrosion;

Methodology

Initial experiment would be conducted in TGA (STA 449 F1 Jupiter). Nanosized ZnO is selected as study objective in order to validate the particle size effect existence in the ZnO sulfation reaction.

Also, the reported experiments of sulfation reaction were typically conducted in a fixed bed reactor, varying temperature, and concentrations of SO_2, O_2 and H_2O.

Acknowledgements

The author would like to express her gratitude to the China Scholarship Council (CSC) and DTU Chemical Engineering for funding this project.

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Phenomena-based Process Synthesis-Intensification

(October 2016 - October 2019)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Contribution to the UN Sustainable Development Goals

Innovation in the current methodos, tools and techniques are key forward for the chemical and biochemical industry to generate more sustainable and economic solutions. Process Intensification (PI) approaches holds the potential to fulfil this objective. In particular bottom-up approaches within PI, operating at lower level provides an opportunity to access the whole search space generating not only intensified but also many novel solutions. This kind of innovation in chemical and biochemical processes brings gains in terms of higher efficiency, economics and sustainability.

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Abstract

This short communication presents the development and application of systematic framework to perform direct and indirect phenomena-based synthesis-intensification, generating novel and intensified solutions without pre-postulating the possible equipment alternatives. The fundamental pillars of this framework are definition and use of phenomena building blocks (PBBs) that includes all possible phases (spanning vapor, liquid and solid), identification of principle PBBs using thermodynamic insights that are combined using the combination rules and generation of the phenomena-based superstructure that can systematically identify potential novel and intensified flowsheet alternatives. The generated flowsheet options are ranked based on Enthalpy Index (EI) to identify potential alternatives for detailed analysis. One of the key features of this framework that distinguishes it from preceding methods is that it is capable of not only generating more economic, sustainable and novel intensified solutions for an existing process flowsheet (indirect synthesis or retrofit) but also allows the simultaneous direct synthesis-intensification by generating phenomena based superstructure using phenomena-based approach without any prior information about the process.

Introduction

In order to meet ever-growing demands, chemical and related industries are constantly looking for the solutions that are economical, sustainable, efficient, and are easily applicable and scalable. The major challenges while achieving these objectives are:

- How systematically, the required innovative and sustainable solutions can be achieved?
- How different solutions can be efficiently and quickly screened and assessed?
- How complexities of industrial processes can be managed?
- How to achieve guaranteed non-trade off solutions from an environmental, technical and economic perspective?

Thus, in recent years, a major focus in the process technology has been on hybrid/intensified and novel equipment significantly improving the performance of chemical and biochemical processes. Therefore, the tools and methodologies that potentially could transform basics of process synthesis and design; generating innovative and sustainable solutions are highly desirable. The key attributes of such methods and tools should be that they are systematic, flexible in applicability and approach as well as covering a wide range of domains and scales from molecular to process or from phenomena to the unit operation scale providing novel solutions.

Process Intensification (PI) is one of the many approaches that has enormous potential to achieve mentioned objectives. A recent trend in terms of the holistic PI approaches is use of bottom-up approach that diverts from the traditional unit-operation based approaches within process synthesis and process intensification. These approaches are based on the physicochemical phenomena, functions, and/or the building blocks at lower aggregation increasing the search space and generating novel and innovative solutions at higher level i.e. unit-operation level. The research work done in this project is based on the phenomena-based bottom-up approach.

PBS-Intensification: Methodology & framework

The methodology developed to perform phenomena based synthesis (PBS)-Intensification consists of 13 steps across the four stages, algorithms, knowledge bases and few associating tools. An overview of the framework developed for the methodology is given in Figure 1.

In stage I, the main objective is to set up the problem and perform synthesis analysis i.e. defining problem, collecting the reaction information, the raw material and product data, the mixture analysis and generation of binary property ratio matrix. In stage II, the analysis of the base case i.e. existing process flowsheet (if available) is performed. Here, an initial list of tasks and phenomena along with the desired list of phenomena mitigating the process hotspots from the base case is identified. In case of no base case flowsheet, stage II is skipped.

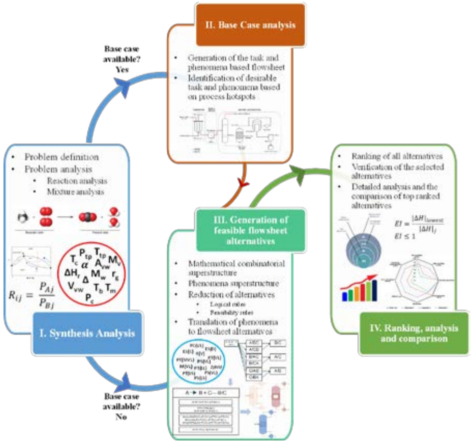

Figure 22: An overview of PBS-Intensification

In stage III, firstly a mathematical combinatorial superstructure of compounds is generated followed by identifying principle PBBs. Further, using total list of phenomena, knowledge bases and algorithms, the phenomena-based superstructure is generated. Further, in this superstructure, alternatives are then reduced by following the logical and feasibility rules. The reduced superstructure consisting of principle PBBs is then translated to the basic structures and thus using combinatorial algorithms and translation of the basic structures to unit operations, potential flowsheet alternatives are generated. Then, in stage IV, the flowsheet alternatives are ranked based on Enthalpy Index (EI) to identify the top alternatives which are further analyzed to identify potentially innovative and intensified solutions.

Case Study: Production of Dimethyl Ether (DME)

DME is categorized as a green energy source and the demand for DME continues to increase as it is expected to reach 11.72 billion USD by 2023. In this case study, novel and intensified solutions for the production of DME from methanol are generated.

In stage I, the problem type, i.e. direct synthesis-intensification is identified as in this case study no base case flowsheet has been selected. Further, the reaction and related information is collected for the production of DME [1]. The problem is analyzed in terms of the reaction, the pure component and the mixture property analysis to generate the binary property ratio matrix. Alongside, presence of any azeotropes, miscibility gaps and eutectic points are also checked. In this case study no such conditions were identified. The stage II is skipped as there is no base case selected for the production of DME. In stage III, using total number of compounds presents at the reaction outlet (Methanol, DME and water), a mathematical combinatorial superstructure of the compounds is generated. Then using information from stage I, a list of principles PBBs is identified. These PBBs are combined with the mathematical combinatorial superstructure of the compounds to generate a phenomena-based superstructure. The superstructure is reduced by following logical and feasibility rules. The PBBs present in the reduced superstructure are translated to the basic structures which are further combined to generate 3 level of superstructures. These are translated to equipment based flowsheet alternatives which are ranked in stage IV on the basis of Enthalpy Index (EI) values. An overview of number of alternatives generated at different steps of framework is shown in Figure 2.

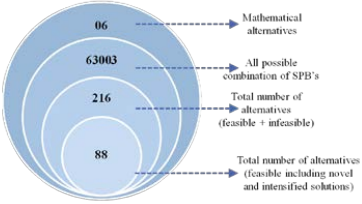

Figure 2: Alternatives generated at different steps

The alternatives selected for further analysis are: Reactive membrane (vapor) distillation – Level 3 with EI-0.462 (alternative 81), Membrane (vapor) reactor → Adsorption – Level 2 with EI-0.961 (alternative 74) and Reaction → Distillation → Distillation – Level 1 with EI-0.33 (alternative 14). These three alternatives are simulated and analyzed in detail to compare the results (Table 1).

Table 2: Comparison of selected alternatives

Parameter	Alt. 81	Alt. 74	Alt. 14
DME Production (kt/y)	~100	~100	~100
RM Cost (M$/y)	61.38	61.51	59.82
RM (MeOH) loss (kt/y)	3.51	3.50	0.05
Energy usage (MJ/hr)	27851.3	23040.0	38878.7
Number of unit-ops	01	02	03
Carbon footprint	7.04E-03	7.02E-03	1.59E-02

Conclusions and future perspectives

The case study shows the capability of developed framework to generate many novel, innovative and intensified solutions without any prior information while operating at the lowest level of aggregation i.e. the phenomena level.

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Design and application of electrochemical sensor for bioprocess monitoring

(January 2019- December 2021)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Contribution to the UN Sustainable Development Goals

Developing analytical approaches in the chemical and biochemical industry for on-line monitoring of processes leads to an increase of productivity. The efficiency of bioprocesses critically depends on the precise control of cultivation parameters. Rapid quantification is required for improved process control. On-line monitoring of the bioprocess enables fast decision-making through applying dynamic feeding strategies that are tailored to the process conditions. It is possible to develop more accurate electrochemical sensors/biosensors, which will lead to more precise on-line measurement of key state variables and metabolites in bio-based processes.

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Abstract

Monitoring and control of fermentation processes is important to ensure high product yield, product quality and product consistency. More knowledge on on-line analytical techniques such as electrochemical sensors is desired in the fermentation industry to increase the efficiency of on-line monitoring systems. This project aims at developing electrochemical sensors and biosensors for the monitoring of ammonium as a key state variable of the fermentation process.

Introduction

Fermentation processes are widely used in the production of food and food ingredients, pharmaceuticals, enzymes, and a number of bulk chemicals. Efficient control of fermentation processes is often essential for obtaining a high yield and relies on timely and accurate information concerning the physical, chemical, and biological conditions in the bioreactor [1]. Today, physical and chemical parameters such as, for example, the pH, temperature, dissolved oxygen concentration, and carbon dioxide evolution rate (CER) are measured reliably on-line, whereas information concerning biologically important variables such as, the concentration of different nutrients, metabolites, and the biomass is mainly available via laborious off-line analyses. Over the past decades, there has been a great effort in developing methods for real-time monitoring of fermentation processes using various advanced sensors [2]. Electrochemical sensors / biosensors offer the possibility of real-time monitoring in combination with the advantages of low cost, high sensitivity and selectivity, and independence of the sample color and turbidity [3].

Ammonium is one of the central nutrients in media for most fermentation processes and needs to be present in relevant levels to promote growth and enzyme production. Besides, there are also major challenges associated with ammonium. It impose additional costs on downstream wastewater treatment if more ammonium is added to the medium than needed by the microorganisms during the fermentation [2].

Specific objectives

One of the objectives of this study is to fabricate an electrochemical sensor, based on polyaniline (PANi) in combination with copper, for the on-line determination of ammonium in the fermentation broth.

An amperometric ammonium sensor is fabricated by immobilization of three different layers on top of a carbon working electrode in a screen-printed electrode (SPE), including electrodeposited copper oxide (Cu_2O), a Nafion membrane and electropolymerized polyaniline (PANi) (Fig. 1). The presence of ammonium causes complex formation with copper, and this causes electroreduction of oxygen to result in an increased current.

Results and Discussion

Amperometry at −0.45 V was utilized for measurement of the response to an increase of ammonium concentration at the PANi-Nafion-Cu-modified electrode (Fig. 2). A consistent increase in the cathodic current was observed as a result of the increased ammonium ion concentration.

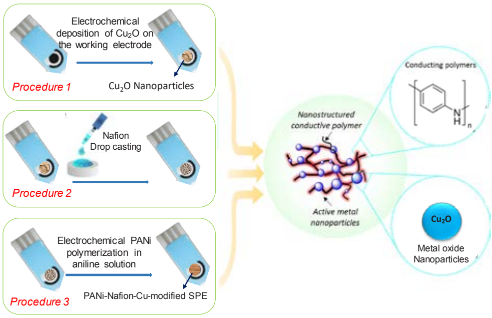

Figure 23: Schematic representation of the fabrication of electrochemical sensor.

The addition of ammonium ions resulted in the formation of a complex between Cu(I) and neutral ammonia, which is easily oxidized by dissolved oxygen to Cu(II) [4] with subsequent electrochemical reduction back to Cu(I), observed as a cathodic current increase. Four electron reduction of oxygen down to water illustrates the high reactivity of the Cu(I)-based catalyst. In other words, ammonia complex formation triggers an oxygen reduction reaction (ORR) at the Cu(I)-based species, which in turn, acts to enhance the binding. The whole process is explained in terms of ammonia-associated ORR electrocatalysis, as illustrated in Fig. 3.

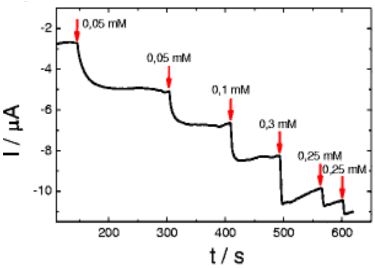

Figure 2. Amperometric response of electrochemical sensor to successive additions of NH_4Cl (−0.45 V, phosphate buffer).

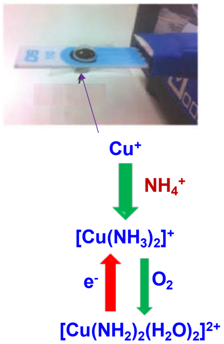

Figure 3. The ORR at the Cu(I)-based PANi composite in the presence of ammonia

Conclusions and future work

An amperometric sensor for ammonium quantification has been elaborated using an ORR catalyst based on PANi in combination with copper. The specific amperometric response to ammonium ions observed at the composite-modified electrode was attributed to ammonia-associated ORR catalyzed by copper centers within the film.

Future work will mainly focus on the integration of electrochemical sensors in sensor particles developed by Freesense ApS that can collect metabolite concentration data in a bioreactor.

Acknowledgements

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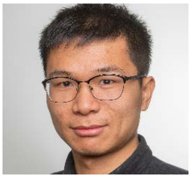
Soft elastomer without chemical cross-linking shows excellent elasticity dominated by Olympic rings and entanglements

(October 2018- October 2021)

Contribution to the UN Sustainable Development Goals

ners with extreme softness can be used as long-term stretchable and implantable devices in different applications, such as soft tissue, sensors and stretchable electronics. Understanding the mechanism of elasticity of the novel elastomers will open the route for molecular design of materials with optimized properties, therefore providing industrial sectors the access to new technical capabilities.



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Abstract

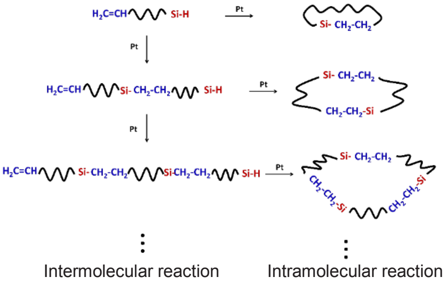
Elasticity of conventional elastomer origins from the elastomer networks formed by cross-links. Recently, an extremely soft silicone elastomer without chemical cross-linking has been shown to exhibit excellent strain recovery from extreme elongation (>5000%), namely 82% after 10 cycles [1]. This observation challenges elasticity of chemically cross-linked elastomers. In this work, the mechanism of elasticity of such silicone elastomer has been investigated. Permanent cross-links formed by concatenated cyclic PDMS (Olympic rings) has been found in the elastomer by swelling experiment and size exclusion chromatography (SEC). Stress-strain measurements and modeling suggested that Olympic rings and entanglements contributed equally to the elasticity of the investigated elastomers.

Introduction

Elastomers display rubber-like elasticity. They can be stretched with elongations of usually 100-800%, and show excellent strain recovery after being stretched. The elastomer elasticity usually origins from the cross-links that connect the polymer chains into an elastomer network [2].

Recently, an extremely soft elastomer with elongation of more than 5000% and recovery of 82% (after 10 cycles) was reported. Different from conventional elastomers, no chemical cross-linking existed in the elastomer [1]. This observation challenges the conventional mechanism of elasticity of cross-linked elastomers, because a material with virtually no cross-links should not be able to recover strain to such extent.

The elastomer was prepared by hydrosilylation reaction from linear polydimethylsiloxane (PDMS) with two end groups of hydride group and vinly group, respectively. Based on the understanding of the reaction, chain extended PDMS and cyclic PDMS are formed by intermolecular reaction and intramolecular reaction, respectively, as shown in scheme 1. Chain extended PDMS can form entanglements, while cyclic PDMS can form concatenated rings (Olympic rings). Entangled PDMS show viscoelastic properties, while Olympic rings can potentially form permanent cross-links, because linkages in the Olympic rings can act as conventional cross-links to form an network [3].



Scheme 1 Possible topologies formed through hydrosilylation reaction.

Specific objectives

The main target of the project is to figure out the mechanism of the elastomer elasticity. Swelling experiments and size exclusion chromatography (SEC) tests were performed to investigate if permanent cross-links exist and how they are formed. Then the modeling of stress-strain curves based on network models was carried out to study the contributions of Olympic rings to the elastomer elasticity.

Results and discussions

The elastomers were prepared from DMS-HV22 (α-monovinyl-Ω-monohydride terminated PDMS, M_n=15.7 kDa). A long term swelling experiment was performed to investigate the extracted sol fraction and the swelling ratio at various swelling time. As shown in figure 1, the sol fraction and the swelling ratio both came to plateaus after swelling for 6 days. The extracted sol fraction was around 20% after swelling for 18 days, indicating the rest 80% fraction was actually gels with permanent cross-links.

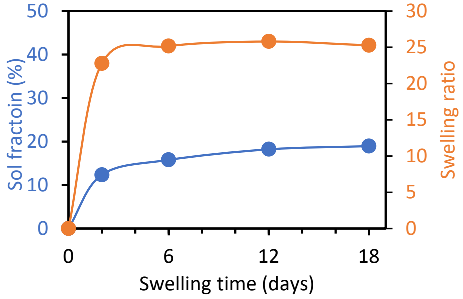


Figure 3: Extracted sol fraction and swelling ratio with swelling time

In addition to preparing elastomers in bulk, they were also prepared in toluene with dilution ratio of 1:1. Theoretically, intramolecular reaction is preferred with dilution. Therefore, if cyclic PDMS is indeed formed during reaction, their fraction will be increased under the dilution condition. This can be checked by SEC. As shown in figure 2, the sol fraction of the elastomer prepared in bulk (red curve) possessed a small shoulder at around 10 kDa regime. The shoulder could be cyclic PDMS, linear PDMS, or their mixture. For the case of dilution (green curve), there was a small peak at the same regime, showing an increased fraction of the small molecules. This was reasonable, because more rings were formed due to the decrease of intermolecular reaction possibility at dilution condition. Furthermore, the green peak located on the left side of the blue peak (for DMS-HV22), also indicates the presence of cyclic PDMS. Therefore, it was concluded that cyclic PDMS were formed during the reaction, and they probably formed Olympic rings that acted as the permanent cross-links to keep the network stable.

Figure 3 shows the fitting results of stress-strain curves based on three network models [4]. Compared to the experimental data, the calculation based on the slip link model showed the best fitting. In this model, the two fitting parameters represent the contributions of permanent cross-links and entanglements, respectively. The fitted values for both parameters were around 0.04 MPa, suggesting that permanent cross-links and entanglements contributed equally to the elastomer elasticity.

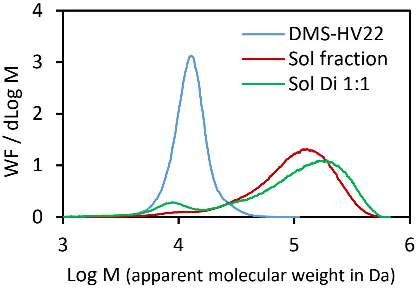


Figure 2: Molecular weight distribution of DMS-HV22 and of sol fractions of elastomers

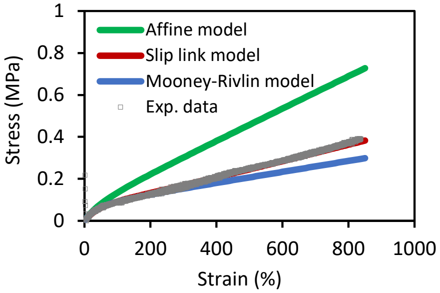


Figure 3: Stress-strain curve and fitting curves based on three different network models

Conclusions

Cyclic PDMS were formed through intramolecular reaction, and they were concatenated like Olympic rings. The linkages in the Olympic rings played the role of the permanent cross-links as in conventional elastomers. Olympic rings and entanglements contributed equally to the elastomer elasticity.

Acknowledgements

The author would like to thank DTU Chemical Engineering and China Scholarship Council for the financial support.

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Membrane-based in-situ product removal

(September 2017- September 2020)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Today, the chemical industry relies heavily on petrochemical feedstocks. To meet the UN Sustainable Development Goals sustainable feedstocks produced from renewable biological sources are required. A potential production method is by fermentation of second-generation biomass into potential building-block chemicals. In many cases however the fermentation metrics yield, productivity and titer are not sufficient for an economic feasible process. Here the synergies between two-stage fermentation and in-situ product removal are investigated to find an improvement in all three metrics.

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Abstract

Fermentation is an attractive technology for producing platform and bulk chemicals, however many products have not seen commercialization due to poor process performance in the three metrics yield, titer and productivity. The synergistic combination of two-stage fermentation and in-situ product removal can potentially improve all three metrics. An extended fermentation time gives better cell utilization and improves the yield, integration with the downstream separation improves the titer and stationary operation during in-situ product removal potentially improves the productivity.

Introduction

The chemical industry has been and continues to be a major emitter of greenhouse gasses. Today, more than 95% of all manufactured products rely on chemistry and conventional petrochemical feedstocks [1]. An often suggested alternative to the petrochemical feedstocks are sustainable platform-chemicals produced via fermentation of renewable biomass [2]. These platform chemicals can then be used in the production of conventional chemical products such as polymers, and valuable fine chemicals. The challenge is that although the fermentation of different platform-chemicals is possible, one or more of three critical process performance metrics, yield (g/g), titer (g product/L) and productivity (g product/(L.h), are unsatisfactory for an economically sustainable production [3].

Often improvements in the three metrics are investigated by and found with cell factory engineering, however a core issue seen in many cases is a low tolerance of the cells towards the xenobiotic products resulting in a toxic response seen as reduced stability, reduced ability to grow and reduced product formation rate [4]. Improving the low tolerance of the cells has proven to be difficult and technical process solutions seems to be required to reach satisfactory fermentation process metrics.

Here the synergistic combination of two known technical process solutions, two-stage fermentation (TSF) and in-situ product removal (ISPR) is investigated to circumvent the low product tolerance and fully utilize grown microbial cells as biocatalysts.

Two-Stage Fermentation

In TSF the growth and product formation has been metabolically decoupled [5], so one can happen without the other. The idea is to overcome some of the issues seen in classical fermentation, where the fermentations can be self-inhibitory as toxic products are produced, and the cells cannot produce more product without also growing.

With TSF the growth phase and the product formation phase of the fermentation has been decoupled and divided into separate stages. In stage 1 the growth is no longer self-inhibitory and in stage 2 the grown cells can keep on producing product at a constant cell concentration as long as the thermodynamics and toxicity of the product allows it. TSF thus has the potential to improve the yield by making more product per cell and improving the productivity by eliminating the self-inhibitory nature of the cell growth.

To further improve the yield cell recycling can be used at the end of stage 2 to have the same cells produce product through multiple cycles of stage 2 before new cells have to be grown. The productivity can be changed by adding a dilution/dewatering step between the two stages.

This gives some freedom in the process design and can potentially improve productivity during stage 2 through dewatering to increase the cell concentration.

A problem still remains though. When the product concentration in stage 2 reaches toxic concentrations and the cells stop producing product the last metric, the titer, remains the same.

In-situ Product Removal

ISPR was proposed as a solution to avoid accumulation of product to toxic concentrations by removing the product from the immediate vicinity of the cells as the product is formed [6]. In practice it is seen as an integration of the first downstream step with the fermentation itself. By choosing a downstream operation with the potential to selectively remove the product ISPR now offers elimination of the toxic response from product accumulation and a higher concentration of product downstream. This integration of fermentation with a selective downstream operation can be used to overcome the mentioned problem of TSF.

Results and Discussion

With the combination of TSF and ISPR several synergies can be found essentially improving the three metrics and the economics of the process.

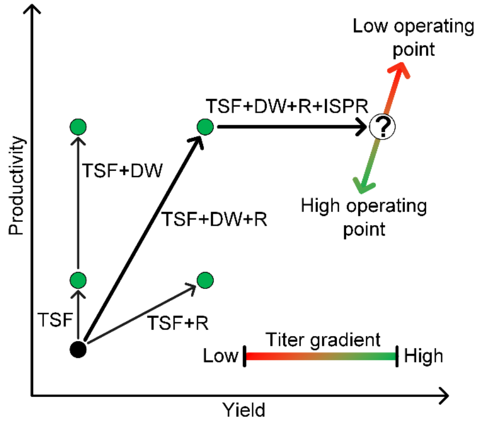

Figure 24: Illustration of the improvements gained with TSF (Green circles) over classical growth-coupled fermentation (Black circle) and the further improvements of TSF with ISPR (?-cirlce). TSF=Two-stage fermentation, R=Cell recycling, DW=Dewatering between stage 1 and 2, ISPR=In-situ product removal. The red-green gradient illustrates the trade-offs seen when choosing the operating point.

The concrete benefits found depends on the operating point of the ISPR-unit, which is when the product formation rate exactly matches removal rate. If the ISPR-unit has a high removal capacity the product concentration at the operating point will be low and vice versa. A low operating point means a higher productivity dictated by the kinetics and potentially a higher yield because of a lower experienced product concentration of the cell. A high operating point on the other hand means a higher downstream product concentration and a higher driving force for the removal and thus an easier separation. Choosing the operating point is thus an economic optimization problem where the CAPEX and OPEX of the fermentation, the downstream separation and the ISPR-unit have to be balanced. The actual benefits of the combination of TSF and ISPR depends on the operating point chosen. The improvements by TSF to classical fermentation and the synergies achieved with ISPR are illustrated in Figure 1.

Very critical to the optimization problem are the time extension of the product formation in stage 2 that ISPR can bring along and the ISPR separation efficiency ($/kg removed).

Extending the product formation time in stage 2 of the TSF is very important for the yield of the process. When the cells can produce product for a longer time the need for growing new cells decrease.

The separation efficiency is a measure of the cost of recovering a kilogram of our downtream product solution. The efficiency becomes very important when the operating point has to be found. If the separation efficiency is low a low operating where the product stream is relatively dilute cannot be afforded. However if the separation efficiency is how the dilution of the product can become almost negligible in the costing of the ISPR-unit.

Conclusions

Combining TSF and ISPR has synergistic benefits that can help realize sustainable production of platform chemicals from renewable biomass. In combining the two the operating point of stage 2 becomes an optimization problem, where effects on the CAPEX and OPEX of the process have to be considered. The operating point is especially sensitive towards the performance of the ISPR-unit and the extension that can be achieved in stage 2 with ISPR.

Acknowledgements

Sino-Danish Center for funding.

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Thermoplastic silicone elastomer

(December 2019- November 2022)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

From daily life to industries, silicone-based rubbers are widely used because they are very soft and tough. However, traditional silicone-based rubbers are not easily recycled due to their chemical structures. In other words, silicone rubbers cannot be melted. As a result, the products are thrown away after use. Therefore, developing silicone-based rubbers that can be melted (or reprocessed) may reduce the waste after use in the future by simply collecting the used materials and re-processing them into new products.

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Abstract

Ureidopyrimidone (UPy) forms very strong dimers through quadruple hydrogen bonds (H-bonds). Therefore, UPys can act as strong physical crosslinkers. Unfortunately, polydimethylsiloxane (PDMS) thermoplastic elastomers (TPEs) prepared only with UPys are rather hard and brittle. However, introducing additional weaker H-bonds by ureas between PDMS chains is expected to yield a soft PDMS TPE.

Introduction

The characteristic mechanical properties of the elastomers (eg. large deformation without failure, short recovery time to original shape as the force is removed) originated from interconnected long-chain molecules[1]. SBS (Styrene-butadiene-styrene) rubber is a representative TPE where the long chains are connected by physical bonds. Such ABA type block copolymers, composed of hard segments (polystyrene) and soft segments (polybutadiene), has been used in industries since the 1960s[2]. In a similar manner, ABA copolymers comprising PDMS as the soft segment have been made as an attempt to make PDMS-based TPEs[3,4,5]. So far, they are rather hard or brittle thermoplastic than soft elastomeric materials. Therefore, supramolecular elastomers based on pendent, associating groups became another approach to prepare PDMS TPEs[6]. For example, UPy has 4 aligned sites that can form H-bonded dimer [Figure 1, c]. In this regard, UPy-bearing PDMS TPEs have been reported[7,8]. However, they are more like thermoplastics rather than soft elastomers or have weak mechanical strength.

Here we demonstrate that using two different types of H-bonds results in soft and tough thermoplastic PDMS-based elastomer.

Specific objectives

Fabrication of a soft PDMS TPE by the combination of the weak H-bond by urea (Figure 1, b) and the strong H-bond by UPy (Figure 1, c).

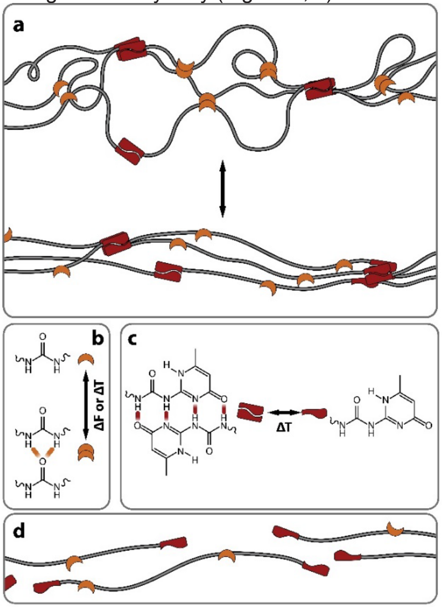

Figure 25: (a) Schematic illustration of the elastomer, (b) hydrogen bond by urea, (c) hydrogen

bond by ureidopyrimidone, (d) dissociation of hydrogen bonds at increased temperature or by organic solvent.

Results and Discussion

The condensation reaction between amine-terminated PDMS ($PDMS-NH_2$) and hexamethylene diisocyanate (HMDI) can increase the chain lengths. In addition, urea H-bonds may form between the chains. The molecular weights of the chain-extended PDMS (PDMS-U) increased as the molar ratio got closer to 1 [Table 1, entry 1-6]. Furthermore, dropwise addition of HMDI into $PDMS-NH_2$ solution led to a further increase in molecular weight [Table 1, entry 7]. All PDMS-U copolymers showed increase in viscosity due to the urea H-bonds. The excess $PDMS-NH_2$ ensure the presence of amine groups at the chain ends for subsequent UPy functionalization.

Table 4: Molar ratio between HMDI and $PDMS-NH_2$ and resulting molecular weight of UPy functionalized PDMS-U.

Entry	Ratio[b]	Molecular weight (g/mol)
1	0	21000
2	0.39	37000
3	0.52	40000
4	0.58	52000
5	0.62	65000
6	0.77	59000
7[a]	0.62	113000

Molecular weights were determined by size exclusion chromatography. [a]HMDI was added dropwise. [b]HMDI:PDMS molar ratio.

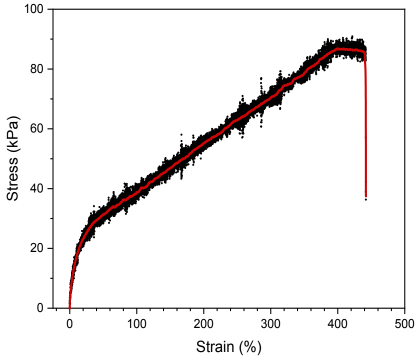

Figure 2: Tensile stress curve (black dots) of the elastomer (Table 1, entry 7) and the smoothed line (red line) by averaging 100 adjacent data points. Elongation rate: 30 mm/min.

Figure 2. shows the mechanical data from elongational test of the UPy-functionalized PDMS-U (Table 1, entry 7). The elastomer was dissolved in a solvent and 20 parts per hundred resin (phr) of silica was added. As the solvent was evaporated, the sample was prepared by hot-press.

Initially, the stress increased rapidly at the low-strain region (below 10 %), where the Young's modulus was calculated to be 150 kPa. This hardening is attributed from the high density of H-bond with entanglements of the backbones[9]. Then the stress gradually increased up to 400 % strain where the reversible H-bonds contributed. However, after this point, it showed plastic deformation. This behavior might be caused from dissociation of UPys as ureas cannot hold the chain backbones any longer under high strain (> 400 %). However, further analyses are required to explain the mechanical behaviors.

Conclusions

A soft PDMS TPE was made by combining two types of H-bonds from urea and UPy. Urea forms weak H-bond that easily breaks under stress. On the other hand, UPy forms strong H-bonds that can hold chain backbones together. The elastomer could be remolded at raised temperature and dissolved in organic solvent by dissociation of UPy dimers [Figure 1, d], which allows green processing and recycling.

Acknowledgements

Funding from Sino-Danish Center for Education and Research are acknowledged.

List of Publications

Not Applicable

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Computer-Aided Design of Sustainable Product Formulations

(October 2016- September 2019)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Driven by obligations to comply with the regulations and various public policies, chemical substitution, is now being widely practiced by industry. Moreover, 'responsible consumption and production', one of the United Nations' seventeen goals for sustainable development, is urging governments, international organizations, the business sector and other non-state sectors and individuals to adopt measures that curtail the use of natural resources and toxic materials as well as the emissions of waste and pollutants over the life cycle of a product so as not to jeopardize the needs of further generations.

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Abstract

The main objective of this project is to quickly and reliably identify promising substitute candidates through model-based techniques and then to verify and evaluate their performance and applicability through experiments. In this way, the experimental resources are used for verification rather than for a trial-and-error search. The overall goal therefore is to investigate comprehensively the uses and properties of the chemicals of concern; develop a systematic framework to identify, compare and select safer alternatives to these, and finally design safe and sustainable chemical product formulations.

Introduction

Numerous hazardous chemicals are found in industrial processes, commodity products and consumer products. Both, humanity and environment are exposed to harmful properties of these chemicals, which have been shown to be detrimental to human health and have adverse effects on ecosystems like loss of biodiversity [1] Therefore, different legislations framed by the regulatory bodies have restricted the use of hazardous chemicals (e.g. Restriction of Hazardous Substances Directive by the European Chemical Agency, EChA [2]). They have also provided various degrees of incentives to substitute such chemicals used in manufacturing processes, equipment operations and formulated products, with environmentally benign and safe alternatives (e.g. EU Chemical Agents Directive, EU Carcinogens and Mutagens Directive). Moreover, reputed organizations have already realized the importance of worker health and safety benefits and have experienced increase in productivity as well as have saved money by simply reducing the use of hazardous chemicals and implementing safer alternatives (U.S. Occupational Health and Safety Administration (Occupational Safety and Health Administration, 2019)). Hence, besides the objective of protecting humans and the environment from the dangers of unsafe chemicals, the regulations imposing chemical substitution have also provided socio-economic benefits.

One area where one can optimize resource consumption as well as find sustainable alternatives to chemical ingredients, is in designing formulated products. Today, the field is typically characterized by an empirical approach to formulation development, almost without the use of theoretical tools, which have a basis in chemical engineering, more specifically, the quantifiable physicochemical properties and thermodynamics. Hence, it is worthwhile to explore the capabilities of such tools in the design of sustainable formulations.

Coating formulations with a liquid delivery system are one of the largest users of organic solvents, many of which are high in toxic volatile organic content (VOC). They are however, extremely useful in protective and decorative functions as they are applied to many types of surfaces, ranging from land-based and marine industrial plants, to ship hulls, to public infrastructure and private homes. The coating can give the coated material improved durability, new functional properties and of course color and gloss. But from the sustainability point of view, the solvents used in the formulation must be environmentally benign and not detrimental to the health of living systems.

A Model-based Framework for Chemical Substitution

A ‘compound of concern’, within the scope of this methodology, is a chemical appearing on the regulatory lists like the REACH ‘Substances of Very High Concern’ (SVHC) list and REACH ‘Restricted Substances List’ prepared by the EChA, any other regulatory list or organic pollutant list. Now, in order to find a substitute for this ‘compound of concern’ the user can follow the Tasks 1 – 8 outlined in the workflow diagram of Figure 1. The data input required to be provided by the user is the chemical name or CAS Number of the ‘compound of concern’. In the case of substitution from a product, the complete product information in terms of the constituents and their composition along with the product-use conditions are required to be provided by the user. Whereas, in the case of substitution of a chemical used in a process or its operation, the complete process description including process operating parameters are required to be provided.

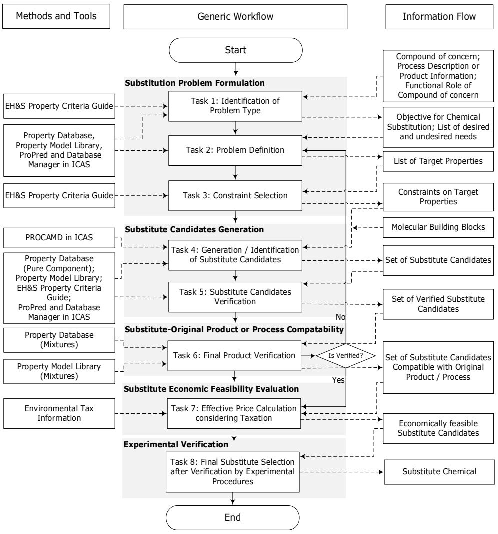

Figure 26: Workflow diagram for the chemical substitution methodology

Coating Formulation Design Methodology

Coatings have a broad range of application in different industrial sectors ranging from marine to domestic where they serve two main purposes: to protect a surface from mechanical, chemical or biological damage when it comes in contact with the surrounding media; and to decorate a surface by adding color or luster and smooth out any irregularities on the surface. The term ‘coating’ encompasses a number of materials like enamels, lacquers, varnishes, undercoats, surfacers, primers, sealers, fillers, stoppers and many others [3]. However, these are all formulated on the same basic principles and contain some or all of the four basic ingredients: colorant, binder, liquid and additive [4].

A formulation design problem can be solved using an integrated experiment-modeling approach [5]. In this approach, predictive models with a wide application range are used to screen candidate ingredients for the product formulation via computer-aided tools. The formulation ingredients and composition obtained from this screening stage are further evaluated using rigorous models or experimental procedures. Making use of this approach, can significantly reduce the resources and time taken to design a formulation when compared to the typical trial-and-error based experimental approach.

Conclusion and Future Work

Current and future work consists of tackling the substitution of chemicals in other types of consumer-oriented chemical-based products, for instance, pharmaceutical products (tablets, inhalers, etc), cosmetic products (creams, powders, lotions) and food products (pastes, granules) that are very important and have wide applications in modern society. But this will also be more challenging than formulations with a liquid delivery system, since care must be taken such that, the introduction of the alternative chemical does not change the lattice structure (e.g. crystalline structure for powders and granules), which in-turn influences the properties like biological activity, friction, adhesion etc. and thermodynamic stability.

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Charge interaction affects the solute transport performance through charged membranes

(November 2018- September 2019)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Ultrafiltration (UF) have been commonly used for purification and concentration in biotechnology, pharmaceutical and food industries due to its advantages of low energy consumption, high efficiency, easy operation and scale up of membrane modules, etc. However, fouling and selectivity limit the usage of this type of membranes. To meet the high industrial requirements standards and sustainable goals, it is essential to improve the UF membrane separation performance and for that, a more in depth study is required to improve and design reliable and efficient UF membranes.

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Abstract

This work encompassed preparation of several membranes with different charge properties using simple polyelectrolytes deposition. Then ultrafiltration was performed using neutral dextran and positively charged lysozyme as model solutes. Permeability, rejection, fouling behavior and charge interaction of different kinds of membranes were further investigated. Our study shows that size exclusion still dominates the transport of charged solutes through the charged membranes when the charge interaction is weak. Furthermore, charge attraction contributes to the severe fouling while weak charge repulsion is advantageous since promotes low fouling and facilitates solute transport.

Introduction

Membranes used for ultrafiltration face two main obstacles: high fouling tendency and low selectivity [1]. Transport of solute in UF membranes is well known to be based on the size exclusion mechanism and efficiency has been reported to be high enough only with a molecular weight difference of 10 times between solutes, which severely limits their application [2]. Numerous studies demonstrated that electrostatic interactions between charged proteins and surface charged membranes can however strongly affect protein transport through UF membranes [3], which could be a promising approach for improving membrane performance in this specific application.

Combining size exclusion and charge repulsion mechanisms along with controlling pH and ionic strength of the protein solution should enable to enhance the performance of membranes compared to the traditional separation in which no charge are involved. Here in this study, we use the layer by layer method for surface modification of commercial polysulfone (PSf) membranes to study the solute transport behavior in the presence of surface charges.

Specific objectives

The scope of the PhD work includes:

- Membrane modification by simple deposition of different polyelectrolytes layers on commercial ultrafiltration membranes
- By adjusting the amount of additives used to promote charge, the charge density can be regulated
- Water permeability, protein flux, rejection, flux decline ratio, pore size of the modified membranes will be studied in detail
- Investigate the effect of size sieving and charge interaction during ultrafiltration process
- Elucidate the charge interaction mechanism between charged solutes and charged membranes
- Evaluate the protocol for commercial membranes modification, such as stability, reuse, cleaning, etc.
- Finally develop a novel, simple, efficient and sustainable modification protocol for membrane surface modification to obtain high performance separation of proteins.

Results and discussion

Water permeability. The pure water permeability decreased from 238.2 L/m^2 h bar to 194.3 L/m^2 h bar after co-deposition of polydopamine (PDA) and poly (acrylic acid) PAA onto the virgin PSf membrane. Despite the PDA layer makes the membrane hydrophilic, together with PAA, it narrows down the pore size of membrane, which could be further confirmed by a significant increase of dextran retention (27.8% to 64.7%). When the positively charged Polydiallyldimethylammonium chloride (PDADMAC) layer was deposited on the PAA+PDA modified membrane, the water permeability further decreased to 108.2 L/m^2 h bar, which was found to be lower than that of the PDA+PDADMAC membrane (157.3 L/m^2 h bar).

Solute flux rejection. The small molecule of lysozyme (14.4 kDa) can easily pass through the virgin PSf membrane (100 kDa), resulting in a low retention of only 7 % (Figure 2). As we incorporated extra layers on the membrane surface, the flux of lysozyme decreased and the retention increased. For the PAA+PDA membrane, the positively charged lysozyme might possibly bind to the negatively charged membrane surface and walls, resulting in the partial pore blocking and increased fouling. In general, the charge modified membrane is expected to exert a high rejection of the same charged solutes, however, lysozyme retention in the positively charged PDADMAC deposited membranes (40% for PDA+PDADMAC membrane and 30% for PAA+PDA+PDADMAC membrane) is less than that of PAA+PDA membrane (50%).

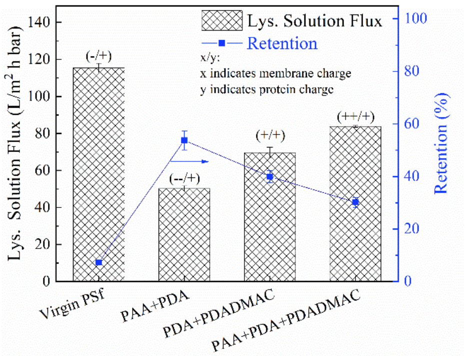

Figure 1. Lysozyme flux and retention using virgin and modified membranes

Flux decline ratio and fouling behavior. The PAA+PDA membrane shows the largest flux decline ratio of 80% in Figure 2, indicating that severe irreversible fouling occurs, which is consistent with the lysozyme retention showed above. In contrast, the PAA+PDA+PDADMAC membrane shows the a lowest flux decline ratio of 35%, suggesting that little lysozyme was adsorbed on the membrane surface or walls due to the charge repulsion.

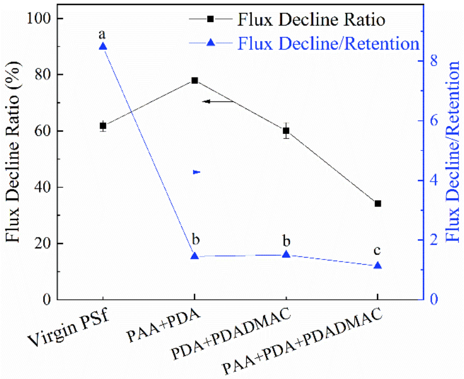

Figure 2. Flux decline ratio after lysozyme filtration and index of flux decline versus retention. The letters a, b, c represent significant differences. Means with different letters are significantly different (ANOVA, $p < 0.05$).

Conclusion and future work

We modified commercial polysulfone membranes using polyelectrolytes deposition and found that weak charge repulsion contributed to low fouling and low rejection while charge attraction resulted in severe fouling. Future work will evaluate the performance of these membranes to separate compounds which have similar molecule weight but different charge.

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CFD-based Optimization of High Temperature Melting Cyclones used in Stone Wool Production

(April 2018- June 2021)

INDUSTRY, INNOVATION AND INFRASTRUCTURE

Contribution to the UN Sustainable Development Goals

In the quest for a sustainable environment there is a large task in reducing the energy consumption and emissions from industrial processes, especially the more energy-intensive industries e.g. glassmaking and melting and smelting.
The work performed in this PhD should assist the development of the new melting process and thereby accelerate the switch away from the older less efficient processes thereby reducing the energy demand and emissions from the industry.

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Abstract

The focus of this PhD project is the development of a Computational Fluid Dynamics (CFD) model for simulation of melting cyclones used in the production of stone wool. The validated CFD model will be applied to evaluate the influences of fuel properties and operating conditions on melting cyclone performance, and to optimize the operation and design of melting cyclones.

Introduction

Stone wool is produced by melting raw materials and subsequently spinning the 1500 ^{o}C melt into fibers using a cascade spinner [1].

Melting of the raw materials has traditionally been done in a cupola furnace with the necessary heat obtained by coke combustion.

This PhD study examines a new cyclone based melting technology developed by Rockwool; the Integrated Melting Furnace (IMF).

In the IMF, raw materials and stone wool waste are blown tangentially into a melting cyclone along with pulverized coal, air, oxygen and natural gas. This generates a swirling motion inside the cyclone in which combustion of the fuel and heating of the feed takes place. The cyclone motion results in the separation of molten particles and the flue gas.

The impact of molten particles on the walls results in the formation of a melt layer that flows down the cyclone and forms a melt bath in the bottom. A conceptual sketch of the melting cyclone is shown in Figure 1.

The technology has an increased energy efficiency and reduced CO2 emission compared to the cupola ovens. However, there is pressure to further increase the efficiency and reduce the emissions (e.g. CO2, NOX). To achieve this better understanding of the process is needed.

Specific Objectives

The aim of the project is to improve the understanding of the physical and chemical processes in the melting cyclone. This will be done through the following steps:

- An integration of fluid dynamic modelling, solid fuel combustion modelling and melting models in a melting cyclone simulation.
- Verification of model performance with experimental data and evaluate melting cyclone performance.
- Investigation of the influence of applying biomass to substitute coal in a melting cyclone and how this influences cyclone performance.

Experimental activity

To verify the CFD simulations experimental data of the process is needed however no experimental studies on cyclones with combustion and melt collection have been found in the peer reviewed literature.

Measurements are therefore performed on full-scale installations at ROCKWOOL factories. The possible measurement types are limited by the hostile environment (i.e. very high temperatures and slagging) in the furnace. Measurements of the flue gas temperature and composition and the heat flux have been performed. Optical measurements are planned.

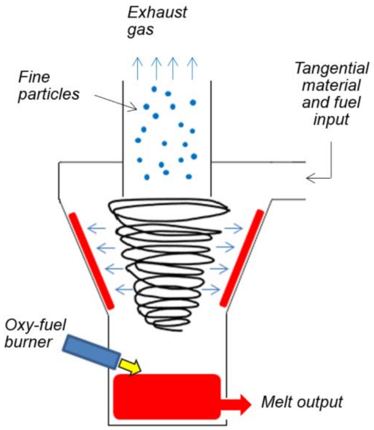

Figure 27: Conceptual sketch of the IMF Melting Cyclone

Modelling methodology

The commercial software ANSYS Fluent is used to perform the CFD simulations of the melting cyclones.

To capture the multiphase reacting particulate flows, a combination of Eulerian and Lagrangian approaches will be used where the Eulerian method is used for the fluid flows and a coupled Lagrangian method is used for raw materials, wool waste and pulverized fuels.

Part of the work will be to test the different existing models for turbulence, radiation, and chemical reactions to determine where the need for development is greatest.

The existing models in the software will be modified or extended when needed using User Defined Functions.

Current Results

Analysis of the melting cyclone process has identified the dominant physical mechanisms and a modelling strategy has been formulated based on the capabilities and limitations of the commercial CFD solver.

The weaknesses of the modelling strategy have been identified and plans for improvement have been made. One of these weaknesses is the available combustion models which is limited to the Eddy Dissipation/Finite Rate model. Work has been done to modify the model to better predict the combustion behavior in cases with oxygen-enhanced combustion.

CFD simulations have been performed with gas and coal combustion, particulate flows and melt flows. First isolated and later combined.

Coupling of particulate and melt flow has been implemented using the Discrete Phase Model and the Volume of Fluid models. This approach has previously been used successfully for slagging coal combustion, see [2].

Raw material melting dynamics have been defined and implemented.

Conclusions and future work

It is possible to combine the relevant physics of the process in a single simulation although some aspects will not require simplifications.

The next step is full scale simulations at the current stage of development and comparisons to the available experimental data.

Acknowledgements

This PhD project is a collaboration between the Combustion and Harmful Emission Control (CHEC) Research Centre at DTU Department of Chemical Engineering and ROCKWOOL International A/S. The financial support from Innovation fund Denmark under Grant number 7038-00191B is gratefully acknowledged.

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Long-term stability of silicone elastomer coatings

(February 2018 - February 2021)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Silicone elastomer coatings are well known for their high thermal and oxidation stability, flexibility and hydrophobicity, their low surface energy and their biocompatibility. Materials protected by silicone elastomer coatings have therefore longer lifetime, which reduce material consumption. As a consequence, silicone-based elastomers find use in e.g. environmentally friendly anti-fouling coatings. Antifouling coatings protect a ship hull from adhesion of marine organisms. A ship without marine organisms on its surface has lower friction, which significantly reduce fuel consumption.

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Abstract

In this work, the long-term stability of silicone elastomer coatings is investigated. The coatings are prepared by a condensation curing reaction between hydroxy-terminated polysiloxane and trimethoxysilane-terminated polysiloxanes. The long-term stability of the coating is evaluated by measuring mechanical properties, such as elongation at break and Young´s modulus over time. We show that the network stability is significantly influenced by chain length and concentration of the cross-linker.

Introduction

Silicone elastomer coatings possess high thermal and oxidation stability, high flexibility and hydrophobicity, and low surface energy. [1] Due to these properties, they are commonly used as protective coatings for example on ships and offshore structures. In order to ensure longevity and efficiency of the involved products, an improvement of the mechanical properties of silicone elastomer coatings is always desirable. The most common methods for the improvement of the mechanical properties are either through addition of fillers or via chemical modifications. Nevertheless, these modifications often come together with deterioration of some of the favorable properties.[2] In this work, we focus on the possibility to improve mechanical properties of silicone elastomers without fillers addition or chemical modifications. The main attention is paid to the connection between silicone network structure, mechanical properties, and long-term stability. From the different types of silicone elastomers, we chose to work with the condensation curing type. The condensation curing silicone elastomers have the ability to cure at room temperature, which is an advantage for protective coatings applications.

Specific Objectives

The objectives of this project are:

- To correlate structure of the silicone network with its mechanical properties and long-term stability.
- Explore possible chemical processes leading to coating instability.
- Design stable condensation curing silicone elastomer coatings with tailored mechanical properties.

Results & Discussions

Silicone elastomer films of around 100 μm thickness were prepared by a condensation curing reaction between hydroxy-terminated polysiloxane and trimethoxysilane-terminated polysiloxane. In order to vary the network structure, the trimethoxysilane-terminated polysiloxane cross-linker was used in different concentrations, and different chain lengths

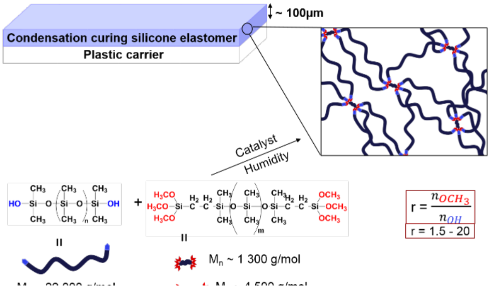

Figure 1: Schematic illustration of the silicone elastomer coating preparation.

(Figure 1). The cross-linker concentration is expressed as the ratio between the OCH_3 of the trimethoxysilane-terminated polysiloxane and OH groups of the hydroxy-terminated polysiloxane. Trimethoxysilane-terminated polysiloxanes were chosen as cross-linkers, because we found commonly used low molecular weight condensation curing cross-linkers, such as methyltrimethoxysilane and tetraethoxysilane, unsuitable for preparation of thin films. Due to the large surface area of the films, non-negligible amounts of these low molecular weight cross-linkers evaporate at a rate comparable to the curing reaction. This negatively influences the stability and reproducibility of the coatings.

Long-term stability of the mechanical properties of silicone elastomers coatings prepared by using trimethoxysilane-terminated polysiloxane cross-linkers are summarized in Figure 2. The cross-linkers of molecular weight ~ 1,300 g/mol and ~ 4,500 g/mol show similar trends regarding the coating stability, where the cross-linker concentration highly influences the elongation at break and the Young´s modulus over time. Specifically, coatings with low cross-linker concentration (r = 1.5 and 2) show a decrease in the elongation at break, and an increase in the Young´s modulus. Such behavior can be explained by unreacted hydroxy-terminated polysiloxane chains, which at first act as a plasticizer, but over time react with sterically hindered methoxy groups of the cross-linker. This assumption was proven by analyzing extracts from the samples, where unreacted hydroxy-terminated polysiloxane chains were found. On the other hand, at high cross-linker concentrations (r = 10, 15, and 20), a steep increase in the Young´s modulus during first days, and a decrease in the elongation at break is observed. We suppose that this is due to reaction between the cross-linker molecules after the hydroxy-terminated polysiloxane is consumed. The most stable coating was obtained using the cross-linker of molecular weight 4,500 g/mol in a concentration r = 5.

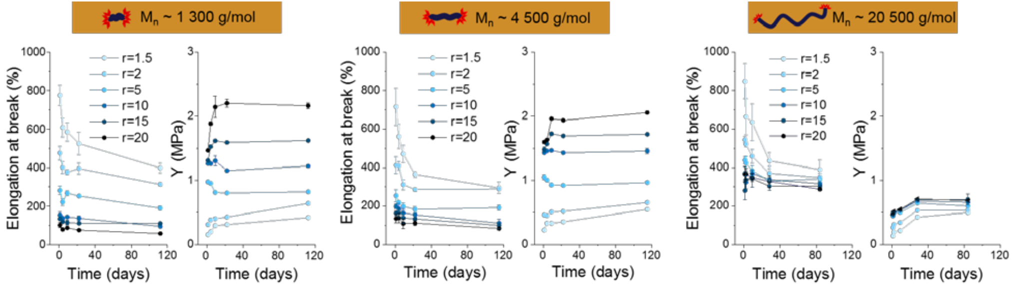

Figure 2: Elongation at break and Young´s modulus (Y) of silicone elastomer coatings over time measured by an ARES-G2 rheometer using SER geometry.

The trimethoxysilane-terminated polysiloxane with the highest molecular weight (20,500 g/mol) shows different trend compared to the first two polysiloxanes cross-linkers discussed above. The coatings show the same tendency in the development of the mechanical properties over time independently of the cross-linker concentration. However, the elongation at break is decreasing and the Young´s modulus is increasing within the first 30 days. After 30 days, the samples show relatively stable mechanical properties. This can be explained by a slow curing process due to poor sterical accessibility of the cross-linker methoxy-groups.

Conclusion

The chain length and concentration of the trimethoxysilane-terminated polysiloxane cross-linker affect not only the network structure, but also the long-term stability of the coating. This is due to both sterical hindrance of the methoxy-groups of the cross-linker and to unwanted reactions between the cross-linker molecules. Taking these two factors into consideration, stable coating compositions, based on the trimethoxysilane-terminated polysiloxane cross-linker were identified. The mechanical properties of these coatings can be tailored by varying the chain length of the cross-linker. Specifically, the softest coatings were obtained using the highest molecular weight cross-linker.

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Acknowledgements

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Evaluation of Single-Pass Tangential Flow Filtration (SPTFF) to Increase Productivity in Protein Purification Processes

(June 2019 – May 2022)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

During the past decades, the global consumption of material and energy resources has increased drastically as a result of economic and population growth. Due to the limited availability of these ressources, responsible consumption and sustainable production of goods becomes increasingly important. This project aims to reduce large volumes in the production of therapeutic proteins, leading to shorter processing times. As a consequence, less consumables are used, less waste is produced, and the production equipment can be downsized, which results in a smaller facility footprint and a lower energy consumption.

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Abstract
Increasing productivity of pharmaceutical production processes becomes more and more important to reduce production costs in order to make drugs available to more people, and to withstand rising cost pressures on the market. Due to the complexity of the purification process of biopharmaceuticals, long processing times and high costs arise. This PhD project aims to increase the productivity of such processes by implementing single-pass tangential flow filtration (SPTFF) as an inline concentration step to reduce large volumes and processing times, and as a result minimize production time, the facility footprint, and the production costs. For the evaluation of this novel filtration technique, modelling and simulation on the process level and on the unit operation level, as well as experiments to confirm simulation results will be performed.

Introduction

As the market for biopharmaceuticals such as monoclonal antibodies (mAbs) continues to rise, it becomes increasingly important to develop cheaper and more efficient production processes. Downstream processing, *i.e.* the purification, of mAbs faces various challenges such as a poor operation flexibility, limited available space, and rising cost pressures. These challenges are caused by larger quantities that have to be processed, the discontinuity of the production, and the inability to scale up certain equipment, among others. Especially large volumes and low product concentrations are a bottleneck in large-scale production due to long processing times and large facility foot prints, which results in low productivities and high costs. Figure 1 schematically shows the different unit operation steps that are part of a typical mAb purification process. To obtain a high-quality product, it is required to process the cultivation raw product containing the pharmaceutical active ingredients (API) through multiple purification steps.

Single-pass tangential flow filtration (SPTFF) is a novel filtration technique which enables the concentration of a product solution in a single pass. SPTFF modules consist of multiple flow stages, each containing multiple membrane cassettes, resulting in a longer flow path, and thus in a longer residence time of the product and a higher concentration factor compared to conventional TFF. The concentration can be done inline before or after every step in a downstream process and has the ability to debottleneck production by reducing large volumes and increasing low concentrations. Figure 2 shows the schematic set-up of SPTFF.

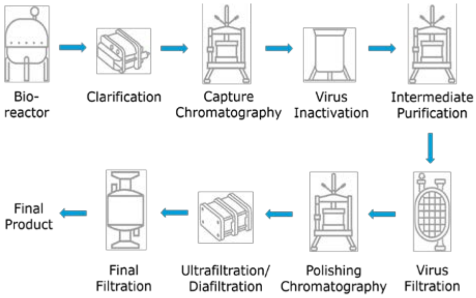


Figure 1: Overview of a typical mAb purification process from the clarification of the cell culture fluid to the final product. Adapted from [1].

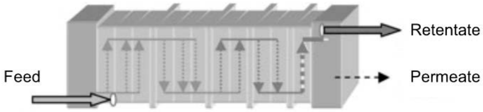


Figure 2: Schematic of SPTFF (3-3-2-2-1 layout) illustrating the flow path of the filtered solution. The concentrated product is contained in the retentate stream. Adapted from [2].

Specific Objectives

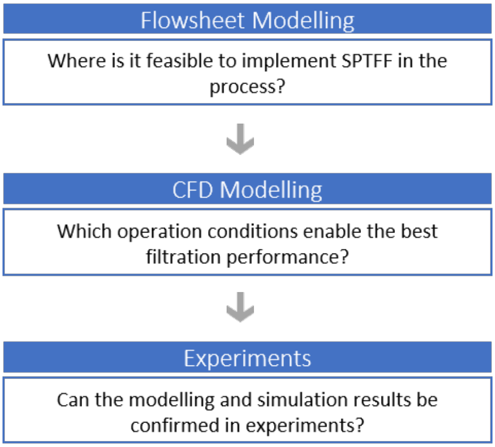
The evaluation of the SPTFF in mAb downstream processes has the following objectives:

1. Modelling of mAb processes and simulation of the implementation of SPTFF in these processes ("flowsheet modelling") using a process simulation software to evaluate where in a process SPTFF can be implemented to improve the process with regards to "kg & h".
2. Modelling of the filtration process on the unit operation level at suitable places in the process using a computational fluid dynamics (CFD) software to define suitable operation parameters and a suitable filter design.
3. Experimental verification of modelling and simulation results.

Workflow

In order to reach the objectives mentioned above, a multi-scale approach is applied to evaluate SPTF. Figure 3 illustrates this approach, which is based on the following three project parts:

1. The first project part depicts the "flowsheet modelling", this means the modelling of the entire purification process. The model is build based on data from existing mAb purification processes. These data allow to make mass balances for every step and the overall process, and to calculate how much antibody is gained and lost in every step. Once a model has been generated which describes the process reasonably well, what-if analyses can be performed. This means that the implementation of SPTFF at different places in the process can be simulated to determine the effect on the process productivity.
2. In the second project part, feasible ideas from the flowsheet modelling are selected and the filtration process is modelled using a CFD software. Subsequently, the effect of different operational parameters such as feed concentration or retentate pressure and the effect of the filter design on the filtration process can be simulated.
3. The last part is to perform experiments in order to verify the modelling and simulation results. If the experimental and computational results do not match, the models have to be refined.


Flowsheet Modelling

Where is it feasible to implement SPTFF in the process?

CFD Modelling

Which operation conditions enable the best filtration performance?

Experiments

Can the modelling and simulation results be confirmed in experiments?

Figure 3: Multi-scale approach applied in this project.

Conclusion and Future Work

Since the project is still in an initial phase, no results are shown in this project description. Once a model is generated, it will be validated, and the implementation of SPTFF at different process positions and combinations of these positions will be simulated. Subsequently, the modelling of the filtration process on the unit operation level will be performed, as well as experiments to confirm modelling and simulation results.

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Coating with inherent sensing functionality based on dielectric elastomer

(February 2018- January 2021)

Contribution to the UN Sustainable Development Goals

Attachment of biofouling to the surfaces of ships, offshore wind farms, and other submerged marine surfaces presents serious economic and ecological problems. Hence, there is need to develop technology which will be beneficial for both marine economy and environment. An environmentally friendly antifouling technology based on silicone coatings is investigated. The coating will involve sensors and actuators and is anticipated to minimize high costs of cleaning damaged surfaces, fuel consumption, use of toxic materials, waste and pollutants which are currently being generated as direct and indirect consequence of biofouling.

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Abstract

Dielectric elastomers (DEs) are soft transducers that can be used as actuators, generators and sensors, due to their ability to deform under mechanical or electrical stimulation. When a substrate-bonded silicone dielectric elastomer is subjected to high voltage, deformations or instabilities in form of creases can be formed at the surface of the DE. In this work, this active deformation of DE surface is used for sensing.

Introduction

Biofouling accumulation on synthetic surfaces, which are exposed to the natural aqueous environment, presents serious problem in a marine industry [1]. High cost of registrations of antifouling coatings containing toxic ingredients, ecological awareness and high cost of cleaning damaged coatings, led to substantial interest in the development of ecologically and economically friendly antifouling technologies. Newest antifouling technologies that are proposed and proof of concept demonstrated, include use of dielectric elastomers, where intentional deformation of the DE is employed to prevent and detach biofouling [1, 2, 3]. These new technologies should replace current antifouling approaches and technologies, which include coatings with controlled release of biocides in order to detach biofouling from the surface.

However, the detection of biofouling on the synthetic surfaces exposed to the aqueous environment, is still visual only. Hence, it is of great interest to add the capability of measuring the efficiency of DE-based antifouling.

Objectives

It is known that when a substrate-bonded DE is subjected to high voltage, deformations or instabilities in form of creases, wrinkles and craters can be formed at the surface of the DE [3,4]. Even though this deformation of DE is limited and not large, it has been demonstrated that it can be used for prevention and detachment of biofouling from the surface of the soft-dielectric elastomer. The underlying idea for this project is that the deformation in the form of creases in the silicone could be also used for detection of biofouling and not only detachment. Therefore, the objective of the PhD project is to fabricate a sensor based on DE, which actively and effectively detects and detaches biofouling from the synthetic surface exposed to the aqueous environment.

The schematic illustration of the working mechanism of the sensor and actuator for the detection and detachment of biofouling is presented in Figure 1.

The sensor acts as capacitor, where one electrode is seawater and other electrode is metal surface of ship or some other submerged metallic marine surface. When high DC voltage is applied between seawater and the bottom electrode, the soft DE is staying in the flat, undeformed state, until certain voltage is reached (Figure 1a). When the critical creasing voltage is reached, creases at the surface of DE are formed. (Figure 1b.). This deformation causes an increase of the capacitance of the device. Further, when the biofoulings are attached to the surface of the sensor, voltage necessary to develop creases at the surface of DE increases, thus the capacitance change. When the biofouling has been detected, further creasing deformation will cause detachment of biofouling from the surface (Figure 1c).

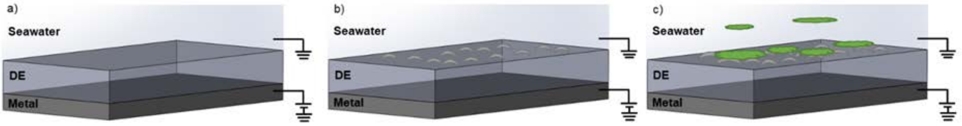

Figure 1: Schematic illustration of the sensor working principle for the biofouling detection and detachment. a) Structure of the sensor (undeformed state). b) Deformation of the top surface of dielectric material ("creased" state). c) Deformation of the sensor, when covered with biofouling. Necessary voltage to produce creases on fouled surface is higher than voltage necessary to produce creases on clean surface.

Experimental

A sensor is made of commercially available platinum catalyzed two-part addition curing polydimethylsiloxane (PDMS) (Ecoflex 00-30, Smooth-on) which was used as dielectric material, coated on a 63.5 μm Kapton polyimide tape that is bonded on to a copper plate. Copper plate acts as an electrode. The silicone film is immersed in a transparent conductive solution (20 wt% NaOH solution) which acts as second electrode. Small hollow cylinder made of poly(methyl metacrylate), which was glued to the top silicone surface, is used as pool for conductive solution (Figure 2.)

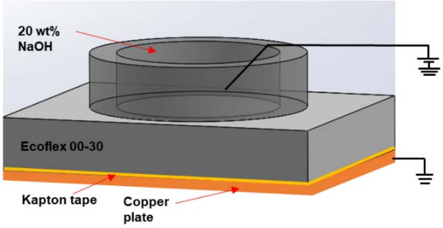

Figure 2. Schematic illustration of the fabricated sensor. Copper is metal electrode in the bottom, covered with Kapton polyimide tape, and coated with Ecoflex 00-30. Conductive solution (20 wt% NaOH) in poly(methyl metacrylate) pool, on the top of the silicone layer acts as second electrode.

The transparent conductive solution enables monitoring of the surface deformation of the silicone under microscope, as a function of the applied voltage [3]. The sensor, which acts as a capacitor was connected in series with a 50 MΩ resistor. This formed a RC circuit which was connected to high voltage power supply. A square wave voltage was applied to the RC circuit and the capacitor charges and discharges with the voltage applied. Therefore, capacitance changes in the sensor are measured as a function of applied voltage, and the threshold voltage at which creases occur when there is an increase of capacitance is identified.

Results and Discussion

Since the membrane is bonded to a rigid substrate, and because elastomers are incompressible, voltages below the creasing threshold create no deformation in the membrane, and therefore no significant change in capacitance. However, when certain value of voltage is reached, instabilities appear at the surface of the silicone in form of creases. This formation of creases increases the capacitance of the device.

Conclusion and Outlook

Future experiments are performed to understand the impact of creasing deformation on the change of the capacitance of the DE. Afterwards, experiments will be performed with attached stiff biofouling layer on the surface of the silicone layer. When stiff biofouling material is attached to the surface of the silicone elastomer, the threshold voltage necessary to develop the creases on the surface of the silicone increases. Measuring the capacitance versus voltage enables identification of the voltage threshold, and therefore monitoring of biofouling.

Expected efficiency of antifouling is demonstrated if biofouling is detected and detached from the surface successfully, and the creases on the clean DE surface again form when primal creasing voltage is applied.

Acknowledgements

This work is part of the Danish Polymer Centre (DPC) and The Hempel Foundation Coatings Science and Technology Centre (CoaST) at the Department of Chemical and Biochemical Engineering at Technical University of Denmark. Financial support from the Hempel Foundation to CoaST.

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NO$_x$ control in combustion of alternative fuels

(September 2017- September 2020)

13 CLIMATE ACTION

Contribution to the UN Sustainable Development Goals

The global energy consumption has increased drastically during the past decades due to industrialization and technological development. The energy has mainly been supplied from fossil fuels, which has caused high levels of air pollution. As a consequence, the world now suffers severely from climate changes. Emission of nitrogen oxides (NO$_x$) is one of the main contributors to air pollution, as it participates in the formation of acid rain and photochemical smog. Therefore, it is important to prioritize development of technologies for NO$_x$ abatement.

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Abstract

Combustion of solid waste fuels in waste-to-energy (WtE) plants is a competitive method for conversion of waste to electrical energy and heat. The emission of nitrogen oxides (NO$_x$) from WtE plants continuous to be a major environmental concern. Additionally, the ash formed during combustion of waste causes severe practical issues due to deposition and corrosion in the boiler. In this project, it is of interest to study techniques for the simultaneous reduction of NO$_x$ emissions, deposition and corrosion in the boiler section of WtE plants. The technique of interest is the selective non-catalytic reduction (SNCR) process using ammonium sulfate as alternative additive. Additionally, it is also of interest to study the impact of inorganic elements, released from the waste during combustion, on the SNCR process.

Introduction

The handling of municipal solid waste (MSW) that is produced daily in large amounts has become a significant challenge. An alternative to traditional landfilling is extraction of energy through combustion in WtE plants.

Most of the waste fractions in MSW are nitrogen containing materials, and thus form NO$_x$ during combustion. The emission of NO$_x$ continuous to be an environmental concern, as NO$_x$ participates in the formation of acid rain and photochemical smog.

In Denmark, the most common technique to reduce NO$_x$ emissions from WtE plants is the selective non-catalytic reduction (SNCR) process using ammonia or urea as reducing agent. The process can achieve up to 40-70% NO reduction in full-scale facilities. The overall SNCR reactions with ammonia and urea are governed by:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6\ H_2O \quad (1)$$

$$NH_2CONH_2 + 2NO + \tfrac{1}{2}O_2 \rightarrow 2N_2 + CO_2 + H_2O \quad (2)$$

The SNCR process is known to be very temperature dependent, and has a narrow temperature window of efficient NO$_x$ reduction, typically located around 850-1100 ^{o}C. It is therefore of practical interest to investigate how the temperature window of effective NO$_x$ reduction can be broadened.

The ash species formed from combustion of MSW have a high tendency to form sticky and corrosive ash deposits in the boiler, due to high amounts of inorganic elements and chlorine in MSW. In previous studies, it has been shown that addition of sulphur containing additives can reduce the extent of deposition and corrosion in the boiler [1]. Therefore, the use of alternative additives in the SNCR process, for simultaneous reduction of NO$_x$, deposition and corrosion, has recently become of interest. Potential additives are e.g. ammonium sulphate and ammonium phosphate. However, fundamental research on the decomposition behaviour of the additives, and their performance in the SNCR process, is required in order to evaluate the viability of the additives.

Specific Objectives

The overall objective of this project is to gain an improved understanding of the NO$_x$ reduction mechanisms within waste combustion. It is of interest to evaluate the use of alternative SNCR additives, such as urea, ammonium sulphate, ammonium phosphate and cyanuric acid, for simultaneous reduction of NO$_x$, deposition and corrosion. **It is also desired to investigate the**

impact of inorganic elements released from MSW combustion on SNCR chemistry.

Experimental Work

A laboratory-scale setup has been developed for the purpose of studying the SNCR process with the use of ammonium sulfate. The main features of the setup, illustrated in Figure 1, include: a homogeneous flow reactor, a feeding system capable of pre-mixing a liquid stream of the reducing agent with a gas stream, and gas analysis by Fourier-transform infrared spectroscopy (FTIR).

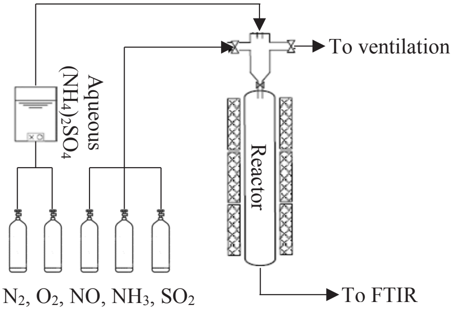

Figure 28: Illustration of the experimental setup.

Aqueous solutions of 2.5 wt.%, 5 wt.%, and 10 wt.% of ammonium sulfate were prepared and added to a closed storage tank of 1.5 L. A 24 V ultrasonic humidifier was placed in the tank for the generation of micron sized droplets of the aqueous solution. The droplets were transported to a homogeneous flow reactor by a N_2/O_2 carrier gas flow. The reactor has an inner diameter of 2.1 cm and a heated length of 45 cm. Additional reactant gases included NO, NH_3 and SO_2.

The flue gas from the reactor was analyzed by FTIR spectroscopy, which measured the gas concentrations of NO, NH_3, SO_2, SO_3, and H_2O. Steady-state NO concentrations were measured with 20 K increments in the temperature range from 973-1198 K. The residence time was 4-6 s.

Modeling Work

A detailed chemical kinetic model for the reduction of NO by ammonium sulfate has been developed. The model is based on the extensive mechanism for nitrogen chemistry developed by Glarborg et al. [2], consisting of a total of 76 species and 534 reactions. The model contains subsets for NH_3, amines, H_2/O_2, H_2S/O_2, and S/N interactions [3].

Additionally, a decomposition model for $(NH_4)_2SO_4$ has been implemented based on recent work by Wu et al. [4]. According to the findings of Wu et al., it is expected that most of the sulphur in (NH4)2SO4 will be released as SO_2 at typical SNCR operating conditions.

Finally, a newly developed subset for NH_2SO_2 consisting of 7 reactions was implemented in the model, as an attempt to describe an observed inhibiting effect of SO_2 on NO reduction.

Results and Discussion

The SNCR performance of $(NH_4)_2SO_4$ was found to be significantly lower than NH_3, as reflected in Figure 2. The optimum temperature was typically observed to be around 1125 K. The low optimum temperature may be explained by the significantly longer residence time in the present setup.

Additionally, the results indicate a strong dependency of SO_2 on the SNCR chemistry, but the model is not able to capture the observed effect, and also overestimates the NO reductions. The low NO reductions obtained by $(NH_4)_2SO_4$ may therefore by explained by the presence of SO_2.

In future work, it is of interest to investigate whether the same effect of SO_2 also applies for shorter residence times, since this will increase the optimum temperature.

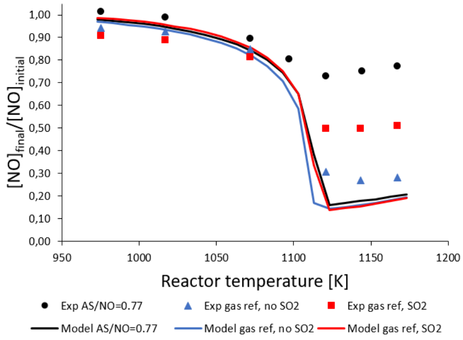

Figure 29: Comparison of experimental and predicted NO reductions using $(NH_4)_2SO_4/NO=0.77$ and $NH_3/NO=1.05$ with an O_2 concentration of 1.25%.

Conclusions

The results of this study showed relatively low NO reductions when using ammonium sulfate, as compared to NH_3. It was also found that addition of SO_2 had an adverse impact on the NO reduction, which may explain the poor SNCR performance of ammonium sulfate.

Acknowledgements

The project has received financial support from the Sino-Danish Center for Education and Research, and Babcock & Wilcox Vølund.

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Role of Additives on Corrosion Protection of Metals by Organic Coatings

(February 2019- January 2022)

Contribution to the UN Sustainable Development Goals

The aim of this project is to investigate the role of the inhibitive pigments in the anti-corrosive performance of organic coatings and the introduction of smart coatings technology for a control-release of the inhibitive species into the organic coatings for corrosion prevention. With the use of nano-containers, active compounds of the coating will be released under demand and losses into the environment will be minimized.

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Abstract

Development of more environment-friendly coatings for corrosion protection of metallic surfaces has drawn great interest in the past few years. Smart coatings have shown promising anti-corrosive performance due to the release of the active compound (inhibitor) of a protective coating in a controlled way. In this project, mesoporous silica nanoparticles have been synthesized and studied as a potential carrier for smart coatings application. Calcium phosphate has been loaded into the nanoparticles as the active compound for the corrosion protection.

Introduction

Organic coatings are employed as an effective way to protect metal structures from corrosion due to their capacity to act as a physical barrier between the metal surface and the corrosive environment [1-2]. However, polymeric films are permeable to corrosive species such as oxygen and water in practice [3]. The protectiveness of organic coatings against corrosion is enhanced by the introduction of pigments. Pigments can be classified into different categories according to their protective mechanism as barrier, sacrificial and inhibitive pigments. The anticorrosive mechanism of inhibitive coatings (coatings embedded with inhibitive pigments) relies on passivation of the metal substrate by the formation of insoluble metallic complexes which work as barriers to aggressive species [4].

Smart coatings have drawn researchers' attention over the past few years and the application of smart coatings has been considered as a novel approach in the field of corrosion protection. In comparison with the conventional coatings where the inhibitors are directly added to organic resins and leach out to provide corrosion protection, smart coatings are able to respond to external triggering like changes in the pH, or mechanical stress, and control the release of certain species from a carrier to provide the as required properties. Several approaches have been developed for the design of carriers: polymer containers, halloysites, nanocontainers with polyelectrolyte shell, layered double hydroxides and mesoporous inorganic materials [5].

Specific Objectives

The main objective of this project is to develop a novel inhibitor for a more sustainable anticorrosive coating design. To do this, the role of smart carriers related to inhibitor performance will be investigated. A fundamental understanding of the underlying mechanism of inhibitor release from smart carriers for corrosion protection and the triggering mechanism will be acquired through experimental studies. Moreover, loaded carriers will be formulated into a coating and the anti-corrosive performance will be tested.

Results and Discussion

Mesoporous silica nanoparticles (MSN) were synthesized by following the Stober method with appropriate modifications. MSN work as smart carriers for the corrosion inhibitor. Figure 1 presents an SEM image of the synthesized nanoparticles. Nanoparticles are spherical with the diameter in the range of 600 to 800 nm.

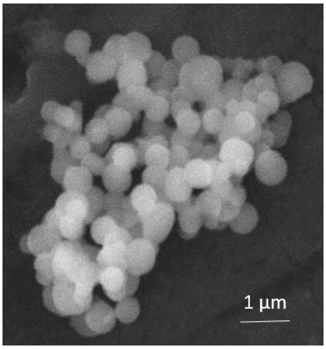

Figure 30: SEM image of the synthesized mesoporous silica nanoparticles**.**

The synthesized MSN were loaded with the corrosion inhibitor –calcium phosphate- under acidic conditions. Because of the mesoporous structure of MSN, inhibitor was able to adsorb into the pores. BET analysis revealed changes in the specific surface area, pore volume and diameter before and after the loading with calcium phosphate. Results for the MSN and the loaded with calcium phosphate nanoparticles (MSN-CP) are presented in Table 1.

Table 5: Textural properties of MSN and MSN-CP.

BET parameters	MSN	MSN-CP
Specific surface area(m²/g)	1285	646
Pore volume (cc/g)	0.9	0.45
Pore diameter (nm)	1.1	0.5

Based on BET results referring to the pore volume loading capacity of the process is calculated. For unloaded particles (MSN) with pore volume of 0.9 cc/g, theoretical loading capacitance is 2.82 g $Ca_3(PO_4)_2$ / g SiO_2. After loading, the pore volume is 0.458 cc/g. Assuming that the inhibitor has filled only the pores, experimental loading capacity is 1.38 g $Ca_3(PO_4)_2$ / g SiO_2. The achieved experimental loading is 48.9% of the maximum. It was reported that mesoporous silica nanoparticles can be loaded up to 70-80 % [6] of the maximum value. In the present work as shown here, it should be noticed though, that the design of the mesoporous silica nanoparticles as well as the loading process that is presented in the current work are not optimized yet.

Conclusions

Mesoporous silica nanoparticles have been successfully synthesized. Loading of calcium phosphate has been achieved under acidic conditions, with the efficiency of 48.9%.

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Financial support from the Hempel Foundation to CoaST (The Hempel Foundation Coatings Science and Technology Centre).

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Quantification of internal stress in thermoset coatings

(February 2019-February 2022)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Thermoset coatings are widely used as anticorrosive coatings in harsh environment. However, curing induced internal stress within coatings can accelerate coatings degradation in service environment. If the influence of coating formulation and curing conditions on curing induced internal stress can be revealed, novel coating formulation and curing procedure can be designed to reduce the internal stress. This can help to produce coatings with prolonged service lifetime giving extended protection of the assets and to save raw materials.

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Abstract

Internal stress can develop within thermoset coatings during the curing process and in some cases, internal stress can be large enough to provoke cracking and coatings barrier performance is severely deteriorated. This project will focus on constructing reliable methods to quantify curing induced internal stress with a cantilever deflection method, exploring the possibility of monitoring localized internal stress with embedded Fiber Bragg Grating sensors (FBGs). Different coating formulations will be used to separate the effect of solvent evaporation process and crosslinking reaction process on internal stress magnitudes. The influence of substrate geometry, including flat substrates and substrates with right angle corner, will also be investigated.

Introduction

Thermoset polymer coatings are widely used as anticorrosive coatings to maintain the service performance of metallic structures in harsh environment due to their excellent mechanical strength and thermal/chemical stability. However, during the curing process, solvent evaporation and crosslinking reactions between binders and curing agents can lead to coating shrinkage and the shrinkage is hindered by strong adhesion at coating-substrate interface, thus internal stress is produced within the coatings [1].

Usually, anticorrosive coatings contain pigments and other additives, and the produced internal stress may concentrate around these pigments and additives at localized areas. The concentrated stress could be surprisingly large and in many cases, it can exceed the coatings fracture strength and provoke crack initiation and propagation [2]. The unexpected development of internal stress and cracks can deteriorate the coatings anticorrosive performance significantly. The barrier property loss within coatings and adhesion property loss at coating-substrate interface may promote and accelerate coatings degradation behavior in service environment, such as coatings delamination, disbonding and cracking [3]. The cracking and disbonding behavior of coatings can leave the metallic devices unprotected and promote localized corrosion, which can result in sudden fracture of structures leading to catastrophic accidents [4, 5].

Researchers have tried to use the "deflection method" to evaluate the influence of binder/hardener type, coating thickness, solvent content, curing temperature/relative humidity variation, and substrate geometry on curing induced internal stress. However, this method cannot measure localized internal stress, which is directly related to cracks formation in coatings, and localized internal stress quantification remains challenging to be achieved [1-3].

Specific objectives

The objectives of this project include:

- To build up a localized internal stress measurement technique
- To reveal the influence of coatings formulation, curing conditions and substrate conditions on the development and magnitude distribution of internal stress within coatings.

- To investigate the relationship between localized internal stress magnitudes and cracks initiation/propagation behavior.

Methodology

The average curing induced internal stress will be monitored with a cantilever beam deflection method. A schematic diagram of the cantilever set-up is given in Figure 1. A climate chamber is used to control the curing temperature and humidity, and the beam deflection distance is monitored with a position detector sensor (Keyence, IL 1000). A CCD camera is positioned to record the deformation of the cantilevers throughout curing process.

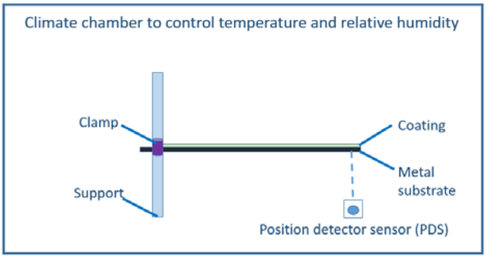

Figure 1: Schematic diagram of internal stress measurement set-up with cantilever beam method.

The localized internal strain will be monitored with embedded Fiber Bragg Grating (FBG) sensors (shown in Figure 2) and the localized stress can be calculated with the strain results obtained with FBG sensors [6].

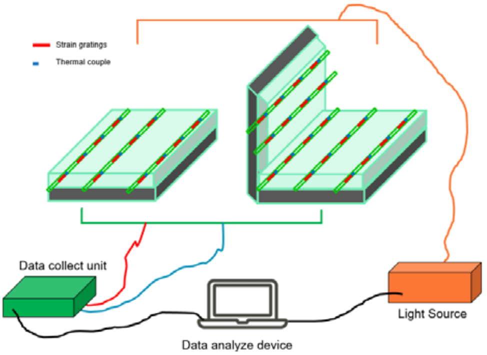

Figure 2: Schematic diagram of localized internal stress measurement method with embedded Fiber Bragg Grating sensors.

To clarify the relationship between coating curing behavior and internal stress development, coatings curing behavior will be investigated. This will include solvent evaporation rate, crosslinking reaction kinetics and coatings mechanical properties evolution (such as modulus and Poisson's ratio) through the curing process.

The influence of curing induced internal stress and micro-cracks resulting from localized internal stress on coatings barrier properties will be investigated with Electrochemical Impedance Spectroscopy (EIS).

Progress and future work

Three types of coatings, i.e. physical-curing coatings, crosslinking reaction curing coatings without solvent, and coatings formed through solvent evaporation and chemical reaction process, have been prepared to separate the influence of solvent evaporation process and crosslinking reaction process on curing induced internal stress. The preparation of coating samples to be used with the cantilever deflection method has been optimized with coatings length and thickness control.

The influence of coatings formulation and substrates geometry conditions (such as flat substrates and substrates with right angle corner) on average/localized internal stress will be investigated together with the relationship between coatings curing kinetics and internal stress development.

Acknowledgement

Financial support from the Hempel Foundation to CoaST (The Hempel Foundation Coating Science and Technology Center).

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Continuous Enzymatic Catalysis: A Framework for Accelerating Industrial Implementation

(November 2017- October 2020)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Contribution to the UN Sustainable Development Goals

As the global population continues to rise, so does the demand for all goods, from pharmaceuticals to fuels. Continuous processing, which has historically been restricted to production of lower value commodity chemicals, increases productivity while reducing cost. However, the sustainability of these production processes must also be improved, which can be done by implementing highly selective enzymes to reduce by-product formation. This research seeks to understand how to operate enzymatic reactions continuously to speed up their implementation.

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Abstract

Enzyme catalyzed reactions are an invaluable tool for the synthesis of active pharmaceutical ingredients (APIs). However, the pharmaceutical industry is shifting in favor of continuous end-to-end manufacturing and so; enzyme catalysis must do the same. Narrow residence time distributions and complete conversion are beneficial for API production, indicating that Continuous Plug-Flow Reactors (CPFRs) are the configuration of choice. However, limitations often encountered when using enzymes may necessitate the use of alternative reactor configurations, unless protein engineering can be used to eliminate them.

Introduction

Enzymes are attractive for the production of pharmaceuticals due to their high stereo-, regio- and enantioselectivities [1]. Additionally, they are non-toxic, biodegradable, produced from renewable sugar resources and often operate at mild conditions. As a result, they are frequently more environmentally friendly, sustainable and cost-effective than conventional catalysts. Historically, enzymes were rarely implemented due to limited selection and availability, high costs and inadequate performance. However, advances in protein and metabolic engineering now allow the rapid production of a growing number of enzymes at far lower costs than were previously possible. As such, enzymatic catalysis is becoming increasingly feasible for industrial implementation [2].

In the past, batch operation was often advantageous for the production of pharmaceuticals due to its versatility and flexibility; however, it is often inefficient due to long downtimes and the need for large equipment, as well as high storage and labor costs [3]. In contrast, continuous processing allows steady-state operation, simpler control, automation and scale-up as well as better mass transfer, which all help to improve reaction efficiency. Moreover, in continuous processes there is no need to store reaction intermediates, which can be toxic or unstable, between unit operations. This generally makes continuous processes more reproducible and reliable than batch processes, which is extremely attractive in the highly regulated pharmaceutical industry. For these reasons, continuous processes are rapidly being developed for both research and industrial application to increase productivity, reduce costs, improve quality and generate less waste [4]. This has lead the pharmaceutical industry to begin shifting away from batch processing in favor of continuous operation. As such, it is imperative that enzymatic catalysis do the same so as not to be left behind.

Reactor selection

Continuous Plug-Flow Reactors (CPFRs) have well defined residence times, allowing reactions to be accurately controlled. Furthermore, the length of the reactor can be selected such that the substrate is completely converted, avoiding the need for complex downstream purification of products from structurally similar substrates. These aspects make CPFRs well suited towards selective continuous production of APIs. However, enzyme limitations such as inhibition, the need for multiple phases and/or pH control often preclude the use of CPFRs due to inhomogeneity in the reactor that results from a lack of mixing. In contrast, Continuously Stirred Tank Reactors (CSTRs) are well mixed, but have broad residence time distributions and cannot achieve complete conversion. Nevertheless, these two reactor types can be combined in a variety of configurations to overcome many of the common bottlenecks of enzymatic reactions, as illustrated by the reactor selection tool we have developed (Figure 1) [5]. This framework should help to simplify the development of new continuous enzymatic processes, by utilizing standardized and well-understood reactor technologies.

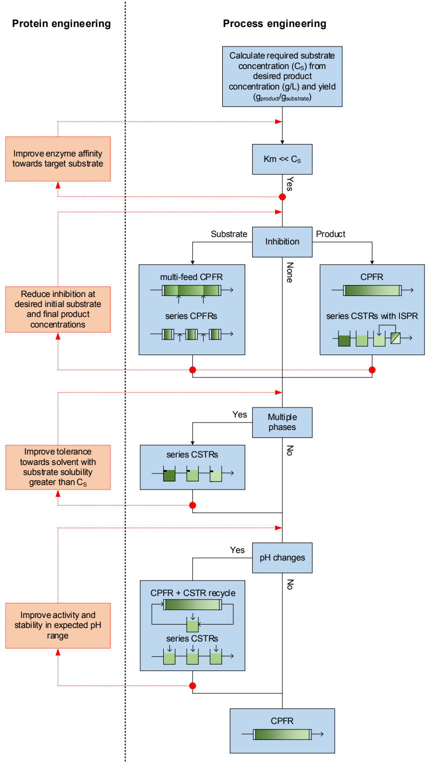

Figure 31: Reactor selection tool for continuous enzymatic reactions, highlighting areas where protein engineering can simplify selection.

Protein engineering

For many conventional chemical processes, careful reactor selection and other process engineering techniques are the only available means of improving performance, since the properties of the catalyst are fixed. However, this is no longer true for enzymes. The advent of advanced recombinant DNA technologies and high throughput DNA sequencing techniques has allowed the properties of enzymes to be modified through changes to their amino acid sequences [6]. Thus, instead of modifying the process to overcome the limitations of the catalyst, the catalyst can be modified to eliminate these limitations altogether, as indicated in Figure 1. This extremely powerful tool sets enzymes apart from other catalysts.

Conclusions

By employing both process and protein engineering in a structured and targeted way, it should become increasingly possible to develop modular, high performance continuous enzymatic reactions that can be seamlessly integrated into existing industrial pharmaceutical production processes. Moreover, performance improvements to enzymes will enable the use of lower, more cost-effective, catalyst concentrations, further accelerating their assimilation into industry. Through standardization, established chemical engineering principles and well-defined technologies, continuous enzymatic catalysis can quickly become an integral part of commercial pharmaceutical production, despite being an emerging field.

Specific Objectives

The aim of this project is to determine whether multiphase enzymatic reactions, specifically biooxidations, can feasibly be operated and modeled in a series of CSTRs, as recommended by the proposed reactor selection tool. Oxygen dependent enzyme systems are some of the most challenging to implement industrially due to their requirement for gas-liquid oxygen transfer [7]. As such, successful demonstration of continuous oxidative enzymatic catalysis would pave the way for the development of continuous processes using other attractive, but complex, enzyme systems, such as those which are cofactor dependent.

Acknowledgments

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Energy Efficient Hybrid Gas Separation with Ionic Liquid

(September 2016- August 2019)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

Absorption and desorption, distillation processes consume significant amounts of energy. With the recent significant increase in global energy demands and every indication that demand will remain high, it is important to consider ways of searching for alternative solvent which they are energy efficient and designing new separation processes which can save much energy. This project is to develop a new ionic liquid-based gas separation technology, taking advantages of some good properties of the solvent, so that the total energy for gas separation could be saved.

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Abstract

Gas separation is one of the common processes in current industries. To realize the goal of being energy efficient, the hybrid separation process, making good use of the advantages in different technology, is applied in this project. Then, for a gas mixture separation, the hybrid scheme where ionic liquid (IL), having the high solubility for specific gas, is used for one component absorption and distillation for the rest gases separation is proposed. However, the enormous number of potential ILs that can be synthesized, makes it a challenging task to search for the optimal one. In this project, a three-stage methodology for ILs screening and process development is proposed. The application of the methodology is highlighted through a conceptual example of a model shale gas separation. Compared with traditional separation technology, the IL-based separation could achieve to be energy-saving and cost-efficient.

Introduction

Gas separation processes have been one of the most important operations in the petroleum, chemical, pharmaceutical, purification and other industries for many years, and this is unlikely to change. Distillation is the main separation method covering 80% of all separation processes within the current industry [1]. Solvent-based absorption and desorption is another common technology primarily for acid gas removal. These unit separation operations, as well as others such as membrane separation, will remain the primary means of gas separation in many industries for the foreseeable future. In order to make good use of the advantages of each technology, the hybrid separation scheme where more than one technology is integrated into a process is usually applied to reduce the total energy consumption.

With some good properties for gas absorption, ionic liquids (ILs) have been widely studied as a potential solvent [2]. Therefore, a strategy for a five-gas shale gas model separation process synthesis where both traditional distillation and IL-based absorption are employed has been developed. However, the numerous combinations of cation and anion make it a challenging task to search for the optimal IL for the shale gas separation. It is necessary to have the solubility data available to assess the potential of an IL for specific gas absorption. Then related separation process could be further developed.

Objectives and methodology

The objective of this project is to develop a hybrid gas separation processing scheme, where IL-based absorption together with other techniques are employed for energy-efficient and cost economic gas processing. We first establish a database containing gas solubility and Henry's law constant in various ILs. Based on this, predicted models including corrected COSMO-RS model and UNIFAC-IL model are developed for the calculation of activity coefficient of gas in new ILs. Then a three-stage methodology for gas mixture separation is proposed. The first stage involves IL screening with two options. One is only based on the experimental database. The other is a computer-aided method which could be used to automatically obtain the optimal IL on the group contribution basis. The second stage is process design and simulation, where the important design issues are determined, and overall separation scheme is generated and simulated. The third stage is process evaluation.

Results and Discussion

As a case study, a five-component shale gas model, which consists of 80% CH_4, 7% CO_2, 7% C_2H_6, 3% C_2H_4, 3% H_2, is assumed. Based on the experimental database, one optimal IL (IL-a: [thtdp][phos]) which has the lowest Henry constant of CO_2 and a higher selectivity of CO_2/CH_4 has been selected. The predicted solubility of other gases C_2H_4 and C_2H_6 in this IL has been calculated with a low solubility based on the corrected COSMO-RS model, indicating the IL can be only used for CO_2 removal process. Through the computer-aided screening method, another IL (IL-b: [MMPy][eFAP]) has also been generated. Based on the calculation of the predicted models, it has a little lower solubility of CO_2 than [thtdp][phos], but a higher selectivity of CO_2/CH_4. Both these two ILs are applied for further simulation to be evaluated. Then, a hybrid separation strategy combining the screened IL-based absorption with distillation is proposed, as seen in Fig.1. Since both the two promising ILs have a high solubility only on CO_2, the solvent absorption method is first applied for CO_2 removing purpose, while other light hydrocarbon gases are separated through traditional distillation. After developing all necessary thermodynamic models for gas-IL systems, the separation processes applying the two optimal ILs are simulated. The simulation results for the two screened ILs ([thtdp][phos] and [MMPy][eFAP]) show a good purity in CH_4 and high recovery rate on CO_2. Then, traditional MDEA based CO_2 removal process is also established and simulated under the same feed condition to be compared.

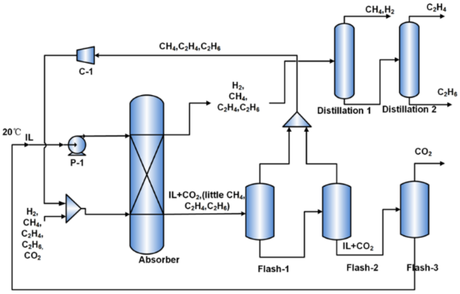

Figure 1: Hybrid IL-based shale gas separation

The two IL-based processes together with the MDEA based CO_2 removal process are evaluated from both energy consumption and economical aspects. The evaluated results can be seen in Figure 2 and 3. Compared with MDEA based CO_2 removal process, both IL-based processes demonstrate a more than 50% energy reduction. The total cost for CO_2 removal in two IL-based processes could achieve to be 11.2% (IL-a) and 38.4% (IL-b), respectively, lower than that in the MDEA process.

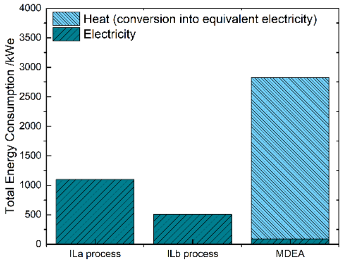

Figure 2: TEC for CO_2 removal in three processes

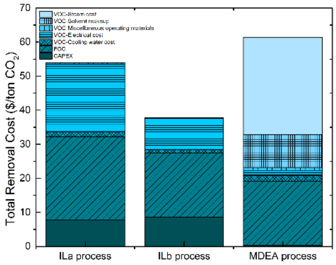

Figure 3: Distribution of total removal cost (TRC) per ton CO_2

Conclusion

This project proposes a hybrid IL-based technology for gas separation process. The three-stage methodology application together with the use of different property models is highlighted through a case study of a five-component model shale gas separation. Two optimal ILs are screened based on experimental database and computer-aided method respectively. Both IL-based process could achieve energy-saving and cost-efficiency. The better performance in both energy and economic aspects in the IL-b based process than that in IL-a provides a foundation of a comprehensive objective-oriented design from molecule to the whole process.

Acknowledge

Financial support received from the joint PhD project from Institute of Process Engineering Chinese Academy of Sciences and Department of Chemical and Biochemical Engineering in DTU.

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Novel silicone-ionic liquid elastomers with remarkable improved electromechanical properties

(December 2017 - November 2020)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

Dielectric elastomers (DEs), which have high flexibility, low weight and large energy densities, are well known materials for advanced electromechanical transducers, i.e. devices that convert electrical to mechanical energy or vice versa. Recently, silicone elastomers have become the favored material for DEs. Ionic liquids are known and sustainable solvents. In this study, a novel silicone-ionic liquid elastomer is shown to be a promising material for highly efficient and environmentally sustainable energy transduction.

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Abstract

The driving voltage for dielectric elastomer actuators (DEAs) is sought lowered for better exploitation of the DE technology, hence an effective way to overcome this shortcoming is to increase their dielectric permittivity. In this study, a novel elastomer with high dielectric permittivity was prepared through the synthesis of silicone elastomer loaded with ionic liquids (ILs). The influence of the amounts of ILs on the electromechanical properties of elastomers was investigated. The dielectric permittivity of the elastomer with 90 phr (parts per hundred rubber) 1-butyl-3-methylimidazolium hexafluoroantimonate ($BmimSbF_6$) was 3.2 times higher than that of the pure silicone elastomer. A simple figure of merit (F^*_{om}) for actuators shows that the elastomer loaded with 90 phr $BmimSbF_6$ was 10.4, thereby indicating that the material has a 10 times better actuation at a given voltage compared to the current reference material.

Introduction

Dielectric elastomers (DEs) represent a promising transducer technology, due to their excellent ability to undergo large and reversible deformations under an applied electric field.[1] Polydimethylsiloxane (PDMS, commonly referred to as silicone) elastomers, which can be operated at a wide frequency range and offer high efficiency and fast response times, are one of the most commonly used materials for DEs. The primary challenge that current PDMS elastomers face is that they require high driving voltages to actuate.[2]

One effective way to reduce the driving voltage is to increase the dielectric permittivity of the DEs. The most common method used to improve the dielectric permittivity of silicone elastomer involves blending a PDMS with high permittivity fillers.[3] Multiple conductive fillers have been used to increase the permittivity of the elastomers.[4] While these methods are efficient in increasing the dielectric permittivity, they also lead to large dielectric losses, and thus no overall improvement. Therefore, it is necessary to find the new fillers to increase the dielectric permittivity while the losses remain constant. Ionic liquids (ILs), which possess high dielectric permittivity and stability, have garnered great interest as elastomer fillers.[5]

The performance of DEAs, when a constant potential is applied, is expressed in a single parameter, a so-called "figure of merit (F_{om})".[2] The voltage applied to transducers is always below the electrical breakdown strength of elastomers. Thus, a simple figure of merit (F^*_{om}) can be used to evaluate the actuation performance of elastomers in practical uses. The equation for the simple figure of merit is given by

$$F^*_{om}(DEA)=\frac{\varepsilon_r}{Y}\Big/\frac{\varepsilon_{r,0}}{Y_0}=\frac{\varepsilon_r}{\varepsilon_{r,0}}\frac{Y_0}{Y} \qquad (1)$$

where $\varepsilon_{r,0}$ and Y_0 are the dielectric permittivity and Young's modulus of the reference elastomer, respectively, and ε_r and Y stand for dielectric permittivity and Young's modulus of the tested elastomer, respectively.

In this study, the ionic liquid $BmimSbF_6$ was added as fillers into PDMS elastomers. The effect of the amounts of IL on the electromechanical properties of elastomers was investigated. A simple figure of merit (F^*_{om}) was used to evaluate the performance of the PDMS-IL elastomers as actuators.

Specific Objectives

This study will be conducted with the following objectives:

1. (1) Study the effect of the amounts of IL on the electromechanical properties of elastomers.
2. (2) Evaluate the actuation performance of PDMS-IL elastomers by a simple figure of merit for actuators.

Results and Discussion

Dielectric spectroscopy tests were performed in order to determine the effect of IL's amount on the dielectric properties. Compared to the pure PDMS elastomer, a significant increase in the relative dielectric permittivity (ε_r) of all PDMS-BmimSbF$_6$ elastomers was observed, as seen in Figure 1. The relative permittivity of elastomers increased with increased amount of BmimSbF$_6$, and relative permittivity of the elastomer loaded with 90 phr BmimSbF$_6$ had increased by 2.2 times compared to the pure PDMS. As shown in Figure 2, the dielectric loss tangent (tanδ) of elastomers with BmimSbF$_6$ has a slight increase in the frequency range from 10^0 Hz to 10^{-1} Hz.

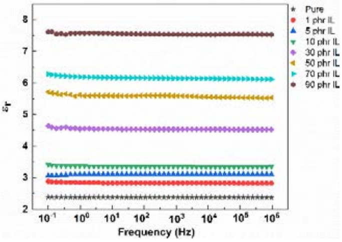

Figure 1. Relative permittivity of elastomers with various amounts of BmimSbF$_6$ at room temperature (RT).

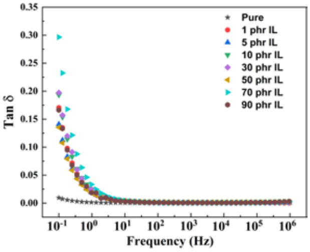

Figure 2. Dielectric loss tangent of elastomers with various amounts of BmimSbF$_6$ at RT.

Elastomers with various amounts of BmimSbF$_6$ were tested to analyze the effect of IL on the mechanical properties. From Table 1, it is clear that the Young's modulus of elastomers with BmimSbF$_6$ decreased with increased amount of BmimSbF$_6$. The tensile strains change only slightly compared to the pure PDMS elastomer when the amount of BmimSbF$_6$ is below 50 phr. Elastomers with 70 phr and 90 phr BmimSbF$_6$ exhibit a small decrease in tensile strains compared to that of the pure PDMS.

The simple figure of merit of elastomers with different amounts of BmimSbF$_6$ can also be found in Table 1. It is clear that the F^*_{om} of elastomers loaded with BmimSbF$_6$ increased with increased amount of BmimSbF$_6$. The F^*_{om} of the elastomer with 90 phr BmimSbF$_6$ is 10.4, which indicates this material has a 10 times better actuation at a given voltage than that of the pure PDMS.

Table 1. Young's modulus, tensile strain and F^*_{om} of elastomers with various amounts of BmimSbF$_6$.

Samples	Young's modulus (MPa)	Tensile strain (%)	F^*_{om}
Pure PDMS	0.49±0.07	318±30	1.0
1 phr BmimSbF$_6$	0.45±0.04	315±20	1.3
5 phr BmimSbF$_6$	0.42±0.09	301±9	1.6
10 phr BmimSbF$_6$	0.40±0.01	297±10	1.8
30 phr BmimSbF$_6$	0.34±0.06	295±20	2.8
50 phr BmimSbF$_6$	0.27±0.06	299±9	4.3
70 phr BmimSbF$_6$	0.20±0.05	267±22	6.6
90 phr BmimSbF$_6$	0.15±0.03	240±10	10.4

Conclusions

In summary, the dielectric permittivity of a film with 90 phr BmimSbF$_6$ was 3.2 times higher than that of the pure PDMS. Compared to the reference elastomer, elastomers loaded with IL became increasingly softer, in line with an increasing amount of BmimSbF$_6$. The simple figure of merit (F^*_{om}) of the elastomer loaded with 90 phr BmimSbF$_6$ was 10.4, showing promising properties for utilization as DE actuator.

Acknowledgements

This study was supported by the Department of Chemical and Biochemical Engineering, Technical University of Denmark and the National Natural Science Foundation of China.

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Modelling of Biomass Combustion and Gasification: from Particle-scale to Reactor-scale

(October 2016 – September 2019)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

Biomass is a renewable energy, which is an alternative of fossil fuel. It can be utilized through thermochemical processes, such as gasification and combustion to produce heat, power and fuels. Computation Fluid Dynamics (CFD) models have been developed to optimize biomass combustion and gasification process for improved efficiency and reduced emissions. To improve the accuracy and computational efficiency of CFD models, efficient and reliable modelling tools in both particle-scale and reactor-scale are needed.

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Abstract

The main objective of this project is to develop efficient and reliable models to simulate biomass combustion and gasification both in a particle-scale and a reactor-scale. Comprehensive single particle models for biomass devolatilization and char conversion have been developed and validated by single particle experiments. Based on the comprehensive single particle models, simplified sub-models for CFD modelling of biomass devolatilization and char conversion have been developed.

Introduction

Computation Fluid Dynamics (CFD) models have been developed to describe biomass combustion and gasification. However, the following challenges remain in both particle and reactor-scale models:

- Particle-scale: biomass devolatilization and char conversion model has been studied extensively at low temperatures conditions (<1473 K) that are relevant for fixed-bed and fluidized-bed reactors. Development and validation of single particle models under high-temperature conditions relevant for fuel combustion are limited. Additionality, the homogeneous reactions in the particle boundary layer are often ignored in current char conversion model.
- Reactor-scale: current CFD modelling neglects particle internal heat and mass transfer, which have significant effects on combustion of large biomass particles [1].

Objectives

The objective of this project is to develop efficient and reliable modelling tools for biomass combustion and gasification:

- Develop and validate single particle models for devolatilization and char conversion
- Develop sub-models for CFD modelling of biomass combustion

Particle-scale model: devolatilization model

A comprehensive single particle model for biomass devolatilization has been developed. The modelling results were compared with our single particle combustion experiment at high temperature conditions. Fig.1 compares the experimental and predicted devolatilization time of pine wood particles with different apparent density (dry basis) and moisture content (6.9 % to 53.0%). Both the modelling and experimental results show that the devolatilization time increases with the increase of moisture content and the apparent density of dry particle. Therefore, particle dry apparent density and moisture content are two critical parameters to determine the devolatilization time, besides particle size and shape, and operating temperature.

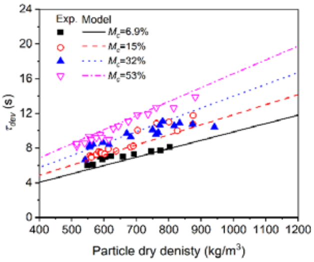

Figure 1: A comparison between the experimental and predicted devolatilization time (d_p=4.0 mm, T_g=1496 K, T_w=1296 K)

Particle-scale model: char conversion model

A comprehensive char conversion model, including heterogeneous reactions (char oxidation and gasification), homogenous reactions in the particle boundary layer, internal and external mass and heat transfer, and particle shrinkage has been developed. Fig.2 compares the experimental and predicted char conversion time of pine wood particles at 1487K with varying O_2 concentration of 0.0 % to 10.5% and H_2O concentration of 25.0%. The predicted char conversion time is in good agreement with the experimental data, when O_2 concentration is 4.4% and 10.5%. However, the char conversion time at 0.0% O_2 is not well predicted, suggesting an improvement of the model, especially the kinetics for steam gasification, is needed.

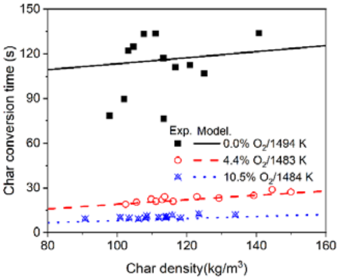

Figure 2: A comparison between the experimental and predicted char conversion time (d_p=4.0 mm, 25% H_2O)

Sub-model for CFD simulation of biomass devolatilization

Coupling the developed comprehensive devolatilization model with CFD is computational demanding. The conventional isothermal particle model commonly used in CFD modelling is only reasonable for small particles. To develop a model with high accuracy and computational efficiency for both large and small particles, a heat transfer corrected isothermal model was developed and more details can be found in Luo et al. [2]. Both the conventional and corrected isothermal models were implemented into ANSYS Fluent® to simulate biomass devolatilization in a batch fluidized bed.

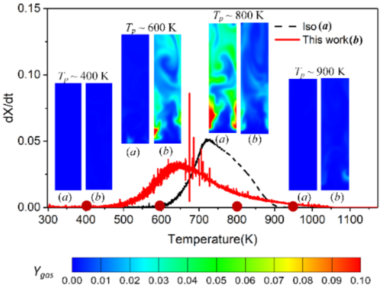

Figure 3: Comparisons of CFD modeling devolatilization rates and a contour plot of volatiles mass fraction (Y_{gas}). (d_p=10.0 mm, T_g= T_w =1173 K)

Fig. 3 shows a comparison of biomass devolatilization rate predicted in CFD simulations. At lower particle temperatures, (T_p~600 K), the corrected isothermal model shows a higher devolatilization rate than the conventional isothermal model. At higher particle temperatures (T_p~800 K), the devolatilization rate predicted by the conventional isothermal model is larger than that of corrected isothermal model. The result is consistent what we observed in single particle modeling.

Sub-model for CFD simulation of char conversion

Similar to the devolatilization model, a mass transfer corrected uniform char conversion model (MTC-UCM) was developed by comparing a comprehensive char conversion model (PCM) and a uniform char conversion model (UCM). Fig.4 compares the predicted conversion history by different models. The results show that the UCM model predicts a much faster conversion rate than the PCM model, while the MTC-UCM can give similar results with the PCM model. The MTC-UCM model also can be easily implemented in the CFD model.

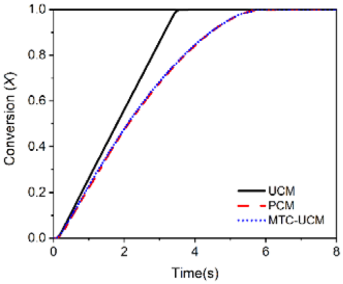

Figure 4: The mass conversion profile history predicted by different models (d_p=1.0 mm, 4% O_2, 13% CO_2, 13% H_2O, T_g=T_w=1173 K, u_s=1.0 m/s).

Conclusion

Comprehensive single particle models for biomass devolatilization and char conversion were developed and further validated by single particle combustion experiments at high temperature conditions. Based on the comprehensive model, a heat transfer corrected isothermal devolatilization model was developed and implemented in a CFD software. The corrected isothermal model both large and small particles with high computational efficiency. A simple char conversion model, which can give similar char conversion profiles as a comprehensive model, was developed. The model can be easily implemented as a sub-model in CFD simulations

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Modular-based in-line coatings production

(September 2019- August 2022)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

The development of the semi-continuous or modular-based in-line production process could represent massive opportunities compared with the traditional coatings production procedure, which would give contribution to reduce the energy consumptions. Besides, lower amount of pigment needed and less waste will be generated during the manufacturing process. In addition, with the help of on-line quality control methods, the time needed for the quality control and correction of the products will be greatly reduced, which means a higher production efficiency.

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Abstract

Moving from the traditional batch coatings production into the new paradigm coatings production procedure represents massive opportunities. For such an improvement, the formulation of coatings product, manufacturing equipment, and the quality control instruments of current coatings industry should be improved. The purpose of this PhD study is to analyze the feasibility of different on-line quality control methods and evaluate the advantages and disadvantages of these instruments. At the same time, the dispersing process of pigments will be studied and a mathematical model will be established.

Introduction

The new paradigm of semi-continuous or modular-based in-line coatings production represents massive opportunities when facing the increasing challenges in the current industry. The overall aim is to be able to produce different volumes of coatings based on the new production procedure.

Two main tasks need to be considered before moving to the new production procedure. The first point is to fully understand the dispersing mechanism of different dispersion instruments, such as high-speed disperser and rotor-stator equipment, and analyze how different pigment agglomerates are dispersed and reach the required particle size. The understanding of the dispersion mechanism can also effectively improve industrial production process and reduce the energy consumption.

On the other hand, such a shift in production methods require better and easier quality control, such as rheology, particle size distribution, colour strength of coatings measurement. The development of the on-line quality control instrument is related to the new production process, which the quality control could be carried out without stopping the production process or manually taking a sample to the laboratory to measure the quality. The on-line quality control methods should perform similar accuracy and stability as the current equipment. Additionally, on-line quality control also presents a chance to not only ensure the final quality, but also be able to monitor the production procedure, which, could lead to lower operation and labor costs, and fewer errors due to human interaction.

Objectives of the project

- Develop a theoretical model to reveal the dispersion process within the high-speed disperser.
- Investigate new and fast on-line quality control methods of evaluating the essential properties of coatings, such as the degree of dispersion, colour strength, and the coating rheology.
- Simulate and analyze different in-line mixing instruments by simulating software
- To design, or construct an in-line coatings manufacturing line based on the simulation result and the selected on-line quality control instruments.

Results and Discussion

New and fast on-line method of evaluating the coating viscosity property was first investigated in this study. Based on the literature study, it was found that several methods could be considered as a possible on-line quality control instrument for coatings production, details about these methods are listed in Table 1.

Table 6: Possible on-line viscosity measurements and their application areas

Methods	Application areas	Reference
Piston-style viscosity measurement	Wire enamel, optical coatings	[1]
Ultrasound measurement	Lubricating oil measurement	[2]
Acoustic sound waver	Food industry	[3]
Capillary rheometer	Household care products	[4, 5]

The viscosity was measured by the advance rheometer, Stormer viscometer, and a specific capillary rheometer. 16 different coating samples were prepared to investigate the performance of the instrument. Figure 1 presents a comparison among these three investigated methods.

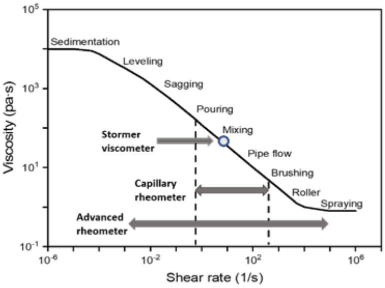

Figure 1: Shear rate analysis range for the advanced rheometer, Stormer viscometer, and capillary rheometer.

It was found that the capillary rheometer could perform a viscosity vs shear rate curve within a certain shear rate range, which could be considered as more precise and reliable equipment than the Stormer viscometer for the quality control in industrial coatings production procedure. However, the advanced rheometer exhibits a much broader measurement range, which is considered as a disadvantage when the capillary rheometer is used in the laboratory development work.

Conclusions

The experiment analyzed whether the capillary rheometer could be used in the industrial production of coatings. Compared with the off-line measurements, the on-line capillary rheometer could be a better choice for industrial coatings production process due to its characteristics, such as efficiency, real-time analysis and reduction of product correction time. However, certain limitations existed for current on-line quality control methods that needed to be considered and resolved.

Future experiments

Future experiments will move to measure the particle size change and viscosity change during the dispersion process.

For most of coatings manufacturers today, the particle size of coatings product is controlled by the fineness of grind gauge, which observes the largest particle size by naked eyes. Although the method could be done within 1 or 2 minutes, this method has a relative large human error. Limitations were also found in other developed methods. Therefore, a proper method to determine the particle size distribution of pigments within coatings system needed to be found in the future experiment.

Mathematical models could be established to describe the particle size change during the dispersion process based on the experimental results. The model will correlate the change in particle size during dispersion with the dispersion time, the rotation speed, and the physical properties of the pigment and solvent, by which, the model could also be used for the determination of the best dispersing parameters.

Acknowledgement

Financial support from Hempel Foundation to CoaST (The Hemperl Foundation Coating Science and Technology Centre).

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Advanced Modelling for Prediction and Control of Related Substances in an Antibiotic Fermentation Process

(September 2019- August 2022)

3 GOOD HEALTH AND WELL-BEING

Contribution to the UN Sustainable Development Goals

This project aims to study the production process of Fusidic Acid, an antibiotic that has seen renewed interest due to the global problem of advancing antimicrobial resistance. By combining biochemical engineering principles and large datasets a computer program is to be created to simulate the production line. This simulation can then be directly applied to the manufacturing of antibiotics. Success of project implementation ensures a healthy supply of affordable medicine to patients who need them.

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Abstract

Production of pharmaceuticals via fermentation is a relatively ill understood process. Even though numerous mechanistic models have been developed focusing on Penicillin, little attention is put on potentially harmful byproducts that hamper product quality. Suitable mathematical models are required to create an optimized process to efficiently meet global demands for high quality antibiotics. This project focuses on a fungal fermentation to produce Fusidic Acid, an antibiotic to treat staph infection. A computer-aided framework is developed based on state-of-the-art biochemical models and large datasets of full-scale production history. The simulation package is then exploited to suggest design strategies to control and monitor the fermentation process to improve manufacturing efficiency with respect to product quality.

Introduction

Fermentation remains a common method in industrial scale production of antibiotics since the development of deep tank fermentation during scale up of penicillin production in 1940s. To serve as many patients as possible with affordable medicine it is necessary to drive manufacturing costs down while increasing the productivity. Accomplishing this requires suitably predictive mathematical models. Penicillin has received a considerable amount of research focused on describing the fermentation process and quantifying the product yields[1-3]. This has allowed researches to develop industrial scale simulation packages that are exploited to deliver highly efficient fermentation processes.

Antimicrobial resistance to penicillin is advancing globally leading to renewed interests in alternative antibiotics. Fusidic Acid is one such antibiotic, which is also produced via fermentation of filamentous fungi[4] and traditionally used to treat staph infections. However, the production process has only been modelled in a lab setting and the kinetics are poorly understood. There is opportunity for development of new and innovative models, not only to predict the production of pharmaceuticals, but also for the first time to predict the production of unwanted related substances that may hamper the product quality and might be potentially dangerous to recipients. The proposed models will be based on modern data driven approach using knowledge-based biochemical engineering principles as well as big data sets.

State-of-the-art

The biotechnological industry increasingly applies mechanistic models due to their significance[5]. Mechanistic models typically consist of differential equations describing the kinetics, built on mass balance, which are solved using numerical approaches. However, biological systems are notoriously complex, so enough knowledge is difficult to obtain. In contrast, modern data driven models require no knowledge of the system behavior and try to build correlations between measured inputs and outputs. The selection of correlation models is vast, ranging from Partial

Least Squares (PLS) to Deep Learning algorithms. Disadvantage of using a pure data driven approach is that they do not contain information on any underlying principles making them unreliable when exploring new designs[6].
In modern times it may be more suitable to build a hybrid model which are constructed using both a mechanistic approach and data driven approach. This is where first principles mechanistic model is constructed with all knowledge incorporated but data driven methods are utilized to support the model to take care of what is not understood[7]. The promising potential of these modeling tools combined with pilot scale validation has been successfully demonstrated for yeast fermentation.

Objectives

The objective of this study is the development of new and innovative models, not only to predict the production of pharmaceuticals, but also for the first time to predict the production of unwanted related substances. The proposed models will be based on modern data driven approach using knowledge-based scientific engineering principles as well as big data sets.
With state-of-the-art science in the field of biochemical engineering combined with laboratory scale experiments a digital twin of the production process is constructed. The digital twin is to simulate the production process on both lab scale and full scale with a high degree of accuracy. The project success criteria are based on:

- Simulation package that simulates and predicts successfully the fermentation process at full manufacturing the scale

- Model predictions are successfully utilized to tune design & operation conditions to improve batch to batch consistency with respect to manufacturing efficiency and quality.

- Model is exploited to suggest monitoring and control strategies to detect and correct deviations in real time.

Successful models developed in this study will eliminate guess work enabling intelligent decision reducing months or years in experimental verification of changes.

Acknowledgements
This project is an industrial PhD project as a collaboration between DTU Chemical Engineering and LEO Pharma A/S. The author would like to thank the Danish Innovation Fund for co-funding the study.

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Sustainable and Cost-Effective Routes for Production and Separation of Succinic Acid

(June 2018- May 2021)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

This project aims to improve a biorefinery process to produce one of the most important products from biomass fermentation: succinic acid. Succinic acid is a biochemical building block used to produce more than 30 commercially valuable products; examples are bioplastics, pharmaceuticals, detergents and food additives. The broad applicability of succinic acid as a chemical building block can both reduce the use of petroleum and be a way to valorize industrial, agricultural and household waste as well as a way to dispose of numerous wastes.

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Abstract

Succinic acid (SA) from biomass fermentation is already a commercial product, however the production costs are still high compared to succinic acid from petroleum and the technological readiness level is not fully developed. Furthermore, while the SA demand is increasing, the biomass-based SA production is far from large-scale bulk synthesis. Most relevant feed-stocks, pretreatments, fermentation and downstream techniques have been identified, and membranes emerge as a key technology in both the production (MBR) and separation of SA. To generate potential and realistic production processes, process simulation, superstructure optimization and lab laboratory experiments are under study.

Introduction

Biorefinery is a promising concept that can contribute overcoming the petrol-era, especially with respect to sustainable fine chemical production, addressing at the same time several problems: the depletion of petroleum resources (with the associated consequences), human sustainability, waste management and political concerns. Production and separation of valuable products from biomass have indeed been successfully achieved and implemented at full scale [1]. However, the lack of cost-effective processes, especially in the downstream, is largely preventing biorefinery products to become economically competitive. Succinic acid from biomass fermentation has gained increasing interest since more than 30 commercially valuable products can be currently synthetized from it, including solvents and lubricants, synthetic resins and biodegradable polymers such as PBS and polyamides, cosmetics, food and pharmaceuticals [1]. Succinic acid has been selected from both the E.U. [2] and the U.S. department of energy [3], among the most important bio-building blocks in biorefinery. Several different technologies are used to produce SA, but standard optimal processes have not been identified yet. Nonetheless, we have identified potential optimal units and working conditions for a cost-effective SA large-scale production [4].

Objectives

Fermentation is a biotechnology from which many valuable bio-products can be obtained however, to economically compete with petrol-based products, cheap feedstocks must be used and, most importantly, both technological advances and process optimization further developed. All the steps required in the production of a biomass-based fermentation product are connected with each other; starting with a certain feedstock for which, specific pretreatments might be needed and both the type of feedstock and pretreatment generating a certain range of compounds. These compounds are nutrients but also inhibitors and both affect the fermentation step, which generates other compounds that need to be removed in the downstream. The selected pretreatment should maximize the production of nutrients while reducing inhibitors. The fermentation should be controlled in order to divert fluxes from unwanted products and finally, the downstream's number of units and efficiency should be reduced and maximized respectively. Thus, the objective of this work is to identify SA production process routes through simulation and ultimately, the sensitive steps resulting from the simulation will be tested and verified trough lab experiments.

Outcomes and working progress

The work started with a literature study that helped to identify the potential feedstocks, fermentation and separation techniques for large-scale production of succinic acid (Figure 1).

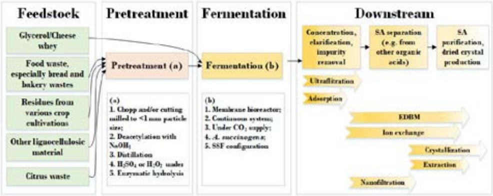

Figure 32: Generic process for succinic acid production listing the most relevant second generation feed-stocks, the proposed pretreatments and fermentation conditions and the optimal range under which major separation techniques can operate.

Inexpensive, sustainable and available feed-stocks were pinpointed (Figure 2), together with the identification of fermentation strategy and microbial strain with the highest records and advantages so far (Figure 1 and Table 1).

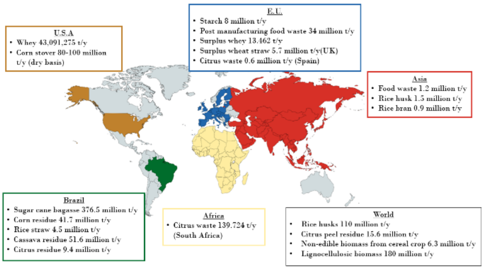

Figure 33: distribution of world food waste that would be suitable for succinic acid production. With the exception for data on rice waste in Asia, which are from the work of Gunarathne et al. (2019) [5], all the other data are based on the work of C. S. K Lin et al. (2013) [6].

These are then studied through process simulation and superstructure optimization, to identify potential best processes for large-scale SA production. Furthermore, the production process of the companies producing SA at commercial-scale were mapped and a techno-economic and LCA analysis are under study.

Experimental configuration

According to the conducted literature study, which includes process simulation on SA production, the downstream is the most expensive step in the whole process [4] and membrane separation and crystallization are key technologies for production of pure SA. Therefore, some experiments were started accordingly, testing the fouling mechanism in membrane separation, which is the biggest problem of this technology. Furthermore, a novel approach combining membrane separation and crystallization emerge from the literature, potentially reducing the number of units in the downstream of SA, where other molecules with similar molecular weights and physicochemical characteristics, e.g. organic acids, are also present.

Table 1. Some collected data for succinic acid production. Used feedstocks, fermentation strategy, productivity and yield.

Feeds -tock	Ferment. strategy	Conc. (g/L)	Product. (g/l/h)	Yield (g g^{-1})
CB	AB	120	1.65	0.805
WS	AB	2.02	≈ 22.5	≈ 0.03
CS	AB	61		0.92
BK	SSF	24.8	0.79	0.28

Abbreviations

Feedstock: cane bagasse (CB); wheat straw (WS); corn stalk (CS); bakery waste (BK). Fermentation strategy: anaerobic batch (AB); solid-state fermentation (SSF).

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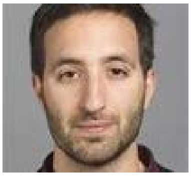
Evaluation of optimization potentials and capacity liberation options in a full-scale industrial wastewater system using a Digital Twin

(February 2018 - January 2021)

6 CLEAN WATER AND SANITATION

Contribution to the UN Sustainable Development Goals

Wastewater treatment is a fundamental pillar for society since it provides a fundamental resource for public health, economic development and environment wellbeing. In this project, we aim to create a Digital Tween (DT) of the largest industrial wastewater treatment plant in Northern Europe. Among others benefits, DT allow *in silico* testing and assessment of new scenarios without the need of spend time and resources realizing them in real life. Nevertheless, the conclusions achieved in computer simulation must be practically reproduced (i.e. piloting) prior to application in wastewater treatment plant. Some of those scenarios can be directed towards improving the operation costs of the wastewater treatment plant, or increase its total capacity.



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Abstract

This abstract shows the preliminary results of applying a digital twin (DT) concept to a full-scale industrial wastewater treatment system (WWS) in operation at the Novozymes production facilities in Kalundborg (Denmark). The DT provides a virtual replica of the plant outline and will enable more informed decisions about how to optimize: Energy recovery, chemical use, operational procedures and capacity liberation. The proposed approach is tested using a dataset comprised of five weeks (06 May 2019 to 10 June 2019). Simulation results show that plant measurements and model predictions range between 5-20 %. The proposed approach is capable to reproduce and describe COD, N, P and particulate removal processes; energy consumption and sludge production. The study will demonstrate a functional plant-wide model of the largest industrial wastewater treatment plant in Northern Europe, including model-aided evaluation of different capacity liberation options.

Full-scale system description

The plant layout consists of a initial buffer tank for influents mixing and homogenization, a primary clarifier for solids removal, a pre-acidification tank for conversion of the heterogeneous organic mixture to short chain fatty acids, two anaerobic granular sludge reactors with two external recirculation tanks which remove organic carbon in form of short chain fatty acids and converts them into a mixture of methane, carbon dioxide and hydrogen sulfide, an activated sludge system comprised of seven aerobic/anoxic units for organics and nitrogen, five secondary clarifiers for biomass recirculation and solids removal, three dissolved air flotation units for non-settable solids removal, two chemical inactivation tanks using calcium oxide for biomass inactivation, and a dewatering station comprised of twelve centrifuges where sludge in thickened prior to transportation to a neighboring biogas facility. Additional details about the plant design and operational conditions can be found in Figure 1. The liquid influents and the reject water coming from dewatering of sludge may be treated anaerobically, aerobically, or using a combination of both.

Digital twin: Main mathematical process model

The digital twin is based on: (1) a biological model, (2) a physico-chemical model and (3) different model interfaces. The biological models comprise an anaerobic digestion model (ADM) and an activated sludge model (ASM). The ADM is used to describe influent conditions, buffer tank, primary clarifier, pre-acidification tank, anaerobic bioreactors, inactivation tank and dewatering, while the ASM describes the activated sludge, secondary clarifiers and dissolved air flotation units. The physico-chemical model includes an aqueous phase + precipitation model and a gas transfer model. Finally, the model interfaces connecting the

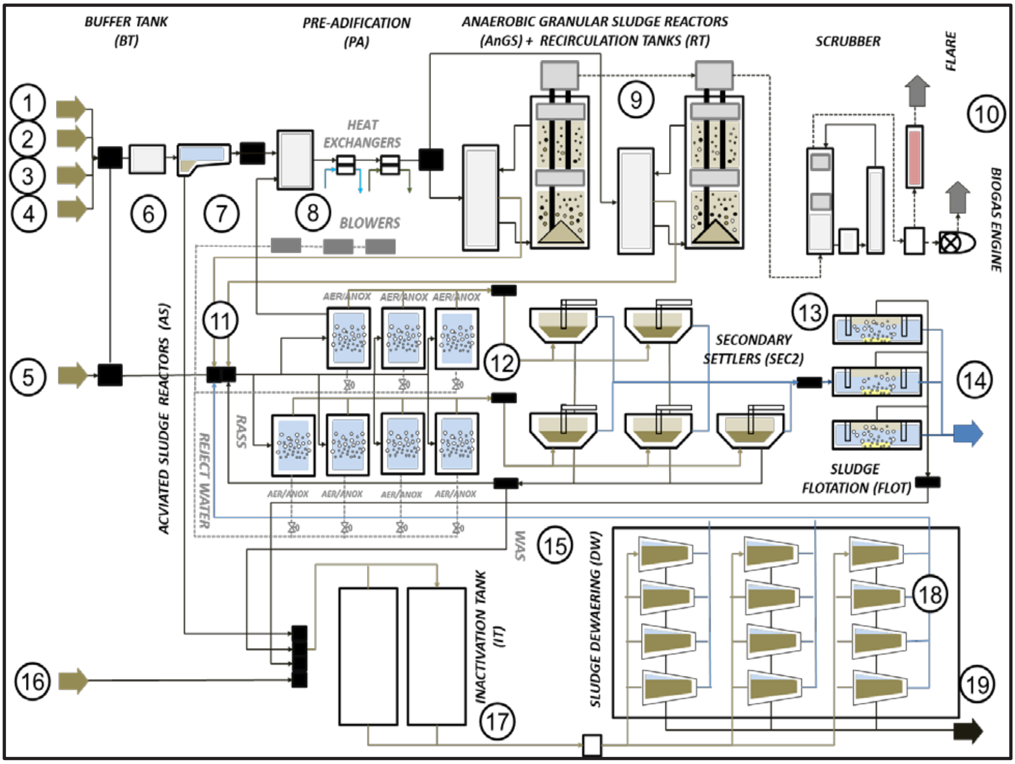

Figure 1. Flow diagram of the wastewater treatment plant under study. Measured and model-predicted streams: **1**, Influent factory 1; **2**, Influent factory 2; **3**, Ethanol stream A; **4**, Ethanol stream B; **5** Influent factory 3; **6**, Buffer tank effluent; **7**, Primary clarifier overflow; **8**, Pre-acidification tank effluent; **9**, Anaerobic digesters effluent; **10**, desulfurized biogas; **11**, Activated sludge influent; **12** Activated sludge effluent; **13**, Secondary clarifiers overflow; **14**, Dissolved air flotation effluent; **15**, Returned activated sludge; **16**, Biomass influent; **17**, Inactivation effluent; **18**, Reject water effluent; **19**, Dewatered biomass effluent.

different moduls. The outputs of the ASM/ADM at each integration step are used as inputs for the PCM module to estimate pH, ion speciation/pairing, precipitation potential and stripping. A comprehensive description of these models can be found in Flores-Alsina et al., 2019.

Conclusions and future work

This abstract has shown the huge potential of digitalization when optimizing water systems by partially showing the preliminary results of an academia-industry collaborative project dealing with capacity liberation in a wastewater treatment plant from the biotech industry. Up to date modelling results are promising, showing a deviation from the measurements of between 5 % and 20%. The project will continue with the modelling of the inactivation and dewatering units as well as the results of implementing different optimization / retrofitting options. CAPEX and OPEX of the different energy/resource recovery and capacity liberation options will be discussed, supported by simulation results obtained with this DT approach. Some of the considered scenarios could be (but not limited to): Anammox technology for to maximize energy recovery in form of methane and reduce energy consumption in the activated sludge; Struvite precipitation for recovery of nitrogen and phosphorous; different biomass inactivation options (technologies, chemicals) and the effect over the entire plant.

Acknowledgments

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In-silico process design and evaluation tool for pharmaceutical manufacturing

(April 2016- August 2019)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Contribution to the UN Sustainable Development Goals

The development and integration of modern and efficient process design tools in early stage pharmaceutical processes is of high importance. It leads towards faster and more economical process scaling and development, while guaranteeing the achievement of previously determined critical attributes for each respective formulated product (in this case, pharmaceutical drugs). Computer-Aided tools and methodologies are the next generation leading implementations for the sustainable and competitive growth and maintenance of this industry.

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Abstract

Pharmaceutical industry faces several challenges and barriers when implementing new or improving current pharmaceutical processes. Moving faster from the laboratory scale to industrial production can be a profitable strategy, but brings many uncertainty to the upstream processes. The objective of this work was to develop, integrate and validate a Model-Based library for the design, simulation, control and integration of laboratory/pilot-plant scale pharmaceutical processes. To this end, the final library was divided into three parts: model collection and integration, critical attributes and uncertainty identification and study, and data-driven control implementation using Radial Basis Functions (RBF) methodologies. The application of the final library was focused on the synthesis and isolation of the Ibuprofen active pharmaceutical ingredient (API), through the Hoechst industrial process.

Introduction

Due to short patent lifetimes, increasing competition from generic manufacturers and strict rules from the regulatory agencies (such as the U.S. Food and Drugs Administration, FDA, and the European Medicines Agency, EMA), the pharmaceutical industry is evolving from a traditions process design approach (with trial and error methodologies) to a model-based aided approach. These changes mostly focus on the implementation of well-known Process Systems Engineering (PSE) methods, with special focus on the delivery of high-quality products while keeping the whole process economically competitive and sustainable. However, due to the need of fast product delivery and reduced time for scaling up, new strategies are needed to the process understanding and drug development, such as the as the usage of principles of chemistry, engineering, material science, and quality control [1]. In addition, as encouraged by the FDA, the use of Process Analytical Technology (PAT) tools to certify and control the end product quality and requirements is of major importance for the whole process risk assessment. This leads to a necessity of implementing fast, reliable and easy to use control strategies and online monitoring, that takes into account or counters previous process uncertainty, occurring at scaling-up implementations. This is especially important when moving from lab-scale to mini-plant or pilot-plant, where time schedules are tight, and downstream processing demands high purity and certain physical criteria (such as specific sizes for crystals, and stable morphologies).

The developed model-based library was implemented in a Matlab/Simulink interface (The MathWorks®, Natick, MA), and focused on the integration of generic pharmaceutical models and data-driven strategies for both process design and process data integration, under upstream uncertainty. The three sections of this library can be resumed into:

-Model collection and integration;

-Critical attributes and uncertainty identification and study;

-Data-driven control implementation using RBF methodologies;

Model collection and Integration

Using the Hoechst Ibuprofen synthesis method as an initial guideline, data and dynamic models for the individual reactions and components was collected and added to the library. The integration of all the collected models and the addition of more generic operations (decantation, hold-up tanks…) allowed the simulation of a daily production of around 240kg of Ibuprofen. The final product quality is high influenced by the individual process units operating conditions, such as changes in the pH, temperature, pressure and proposed catalysts.

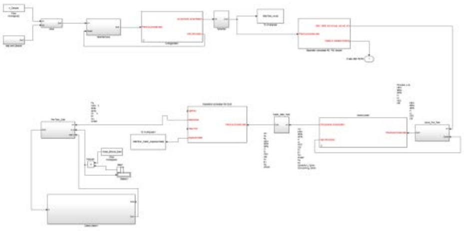

Figure 1: Final flowsheet model of the Ibuprofen synthesis trough Hoescht path. Three reactors are included, as well as a distillation column, a 2-dimension crystallizer model, a decanter and tanks [2,3].

Critical attributes and uncertainty identification and study

For the case scenario, crystal size and size distributions is of high importance. Due to the impact that upstream processes have on the final product, uncertainty and sensitivity analysis implementation are of great importance. The implemented methodologies included local and global analysis, with the latest using Monte Carlo Standardized Regression Coefficients for the quantification of the impact that upstream uncertainty has) [4-7]..

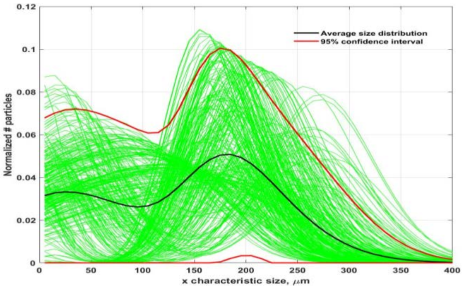

Figure 2: Uncertainty in Ibuprofen crystal size distribution while under upstream deviations, after 5 hours of crystallization.

Data-driven control implementation using RBF methodologies

An RBF Neural Network implementation is included for the integration of online process data with process control [8]. Depending on the availability of online data, different scenarios are proposed [7] (Growing Window, Moving Window and Golden Batch scenarios). The target size and distribution is achieved when severe disturbances are present.

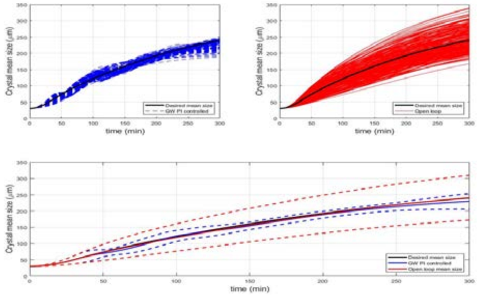

Figure 3: Controlled crystal size (top left), open loop case 8top right) and 95%CI for both scenarios (down) after the use of Monte Carlo with previous reported uncertainty

Conclusion

The developed library has shown great promise for the presented case scenario, and the experimental work developed with the data-driven control library has proven the robustness of the proposed new control methodologies. Future work includes the integration of a component property library, in order to expand the applicability of this library to completely new and non-studied APIs.

Acknowledgments

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An integrated multi-scale framework for bioprocess design, control and analysis

(August 2019- July 2022)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Contribution to the UN Sustainable Development Goals

Developing integrated tools in chemical and biochemical industry for control and monitoring particle processes leads to sustain the resources effectively, in this case flocculation process. The goal of this project aligns with developing a predictive model for flocculation in order to reduce the time required for manual control, unwanted process variations and potential product losses during the operation. In this study it is intended to employ sustainable tools to model the process across the length scale.

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Abstract

The design, control and monitoring of bioprocesses have often always been a serious challenge for industry due to the complexity of the different systems. One of the processes that is being used in downstream bio-manufacturing with different application is flocculation. Despite several applications of flocculation, the mechanism of this process is not well understood. Flocculation is a process that takes place across a broad range of length scales, starting from nanoscale up and beyond microscale. It is essential to develop an integrated framework capable of modeling the system across the scales. In this work, it is aimed to develop a hybrid framework that can model the system across these scales.

Introduction

Flocculation known as a major step in downstream product purification and removing organic biomass and cell debris, has several applications in water and wastewater treatment for clarification, biotechnology in conjunction with microfiltration to improve the efficiency of biological feeds and also in food industry [1]. To develop a an appropriate mathematical model for understanding the kinetics governing the system, it is necessary to studying the stability of emulsion systems [2]. Due to the immense application of this process across the industry, many academic practitioners have put efforts to provide the literature with different kinetic models describing emulsion stability in flocculation [3].

Flocculation as illustrated in Fig. 1 is a process in which, two or more particles of the disperse phase collide and cluster as an aggregate. The process includes aggregation, fragmentation, breakage and erosion phenomena. In this study, the basic mathematical model is used to determine the particle size distribution over the time of the process operation. The first and third terms in Eq. 1 stand for the generation of flocs of size class i due to aggregation of smaller size aggregates and fragmentation of larger size aggregates respectively, while the second term is the destruction of such aggregates due to fragmentation and the rest stands for the destruction of flocs considering breakage and erosion [4].

$$\frac{dN_i}{dt} = \sum_{\substack{j,k \\ \nu_{i-1} \le (\nu_j + \nu_k) \le \nu_{i+1}}}^{j \ge k} (1 - \frac{1}{2}\delta_{j,k})\eta_i \alpha_{j,k}\beta_{j,k}N_j N_k - N_i \sum_k \alpha_{i,k}\beta_{i,k}N_k + \sum_k \gamma_{j,i}S_j N_j - S_i N_i \qquad (2)$$

In order to solve Eq. 1, the normal discretization method is implemented.

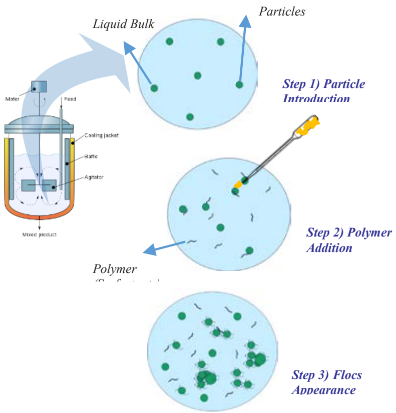

Figure 34: Schematic figure of flocculation process 3 sequential steps

Specific Objectives

In this work it is intended to develop a hybrid framework that uses computational chemistry as the first principles model to determine the surface interactions between the particles in the system. As such, density functional theory is being employed to provide the data required for determination of kernels of aggregation, fragmentation and breakage. Fig. 2 illustrates a representative figure of the sigma surface of a polymer. Polymers are being used a surfactants for flocculation. This sigma surface is necessary to start the calculation of the interactions between polymers as surfactants and silica particles. The machine learning algorithm consists of different hidden layers to train the deep learning algorithm. The population balance model is embedded as one of the hidden layers in the deep learning algorithm. An experimental setup is prepared for collection of data for the model. These inline measurements can provide various floc properties for the deep learning algorithm. Thereby, the machine learning algorithm is fed by molecular simulation data and measurements from experimental setup. The best fitting kinetic expression governing the system then can be found.

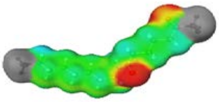

Figure 35: Representative figure of a polymer sigma surface

Results

In this section the image analysis of silica particles flocculation due to the Brownian motion of the particles in the suspension is illustrated**.** Moreover, a time lapse image analysis is carried out to observe the particle size distribution (PSD). Fig. 2 represents the PSD of silica particles after 10 min addition to distilled water with its corresponding size distribution. The experimental setup is being prepared to conduct the core experiments for data collection.

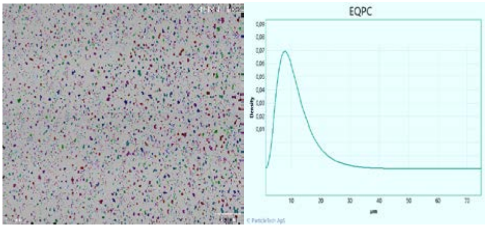

Figure 36: PSD of Silica particles after 10 min in distilled water

Discussion

Silica particles are chosen as the primitive case study for flocculation because the surface chemistry of such particles are well known and the data required for description of their surface chemistry is widely available. Moreover, the image segmentation of Silica particles can be perfectly prepared with the existing image analysis algorithm. Hence, the system can be described in non-observable state and observable scale.

Conclusions

We believe that an integrated hybrid model of computational chemistry and deep learning approaches across the scales helps to understand flocculation mechanism within the corresponding length scales. This model is necessary to provide the system with an automated control strategy which uses model predictive control (MPC) to reduce the time required for manual control and avoid potential product losses during the process operation.

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Novel Catalysts and Reaction Pathways to Complex Nitrile Molecules

(September 2018- August 2021)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

This project contributes to the 12th sustainable development goal. The reason is that it aims to reduce the cost, energy consumption and safety risks of the production of already widely used chemicals. This is done by rethinking the processes and using sustainable feedstocks along with avoiding the use of expensive and low supply precious metals.

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Abstract

Nitriles are important compounds that are useful in many kinds of industries. Especially, acrylonitrile, acetonitrile and hydrogen cyanide are interesting because they are produced on a massive scale. This project looks into finding novel catalysts and reaction pathways to these molecules so that they can be produced in a cheaper and more environmentally friendly way. The study has shown so far that the properties of the catalysts used in this new process can be tweaked depending on the preparative procedure.

Introduction

Whether it is in the production of carbon fiber, nitrile rubber, Lego bricks, or as a solvent or a pesticide, molecules with the nitrile functionality (-C≡N) can be used. Three of the most important molecules with the nitrile functionality are acrylonitrile ($CH_2{=}CHCN$), acetonitrile (CH_3CN), and hydrogen cyanide (HCN).

These compounds are all produced in one process, the SOHIO (Standard Oil of OHIO) process, which have been around for more than 60 years [1]. Since then, the process has been developed to a great extent, but the reaction is the same (Eq. 1).

$$C_3H_6 + NH_3 + 3/2\ O_2 \rightarrow CH_2{=}CHCN + 3\ H_2O \qquad (1)$$

Along with this reaction, HCN and CH_3CN are produced, making it an important source of these compounds as well. Recently, however, the process has suffered from a decline in propylene (C_3H_6) supply and its environmentally taxing nature (with feedstock of fossil origin) [2,3].

Consequently, an alternative process needs to be found. At Haldor Topsoe A/S, they have found that bimetallic catalysts that forms carbides and nitrides upon reaction may well be a part of the answer toward finding this process. Starting with the synthesis of the byproducts, it has been shown that (much more environmentally friendly) methanol can react with ammonia and yield hydrogen cyanide and acetonitrile (Eq. 2 and Eq. 3) [4].

$$CH_3OH + NH_3 \rightarrow HCN + 2\ H_2 + H_2O \qquad (2)$$

$$2\ CH_3OH + NH_3 \rightarrow CH_3CN + 2\ H_2 + 2\ H_2O \qquad (3)$$

The catalyst is comprised of cobalt and tin oxides supported on alumina (Co-Sn/Al_2O_3). The present research project aims at optimizing the processes and the synthesis of the catalysts. This involves efforts in trying to understand the catalytic systems and the support interactions.

Specific Objectives

The objectives of the project are:

- Improvement of the catalysts in terms of catalytic activity, selectivity and stability
- Elucidation of the structural and compositional properties that govern the catalytic behavior and gaining insight into the mechanisms of the syntheses
- Development of kinetic expressions for the reactions

- Economic evaluation of the findings

Experimental

Most of the experiments have been performed at Haldor Topsoe A/S using a setup dedicated to the synthesis of nitriles.

This setup uses a fixed bed (u-tube) reactor and the reactor effluent is analyzed with GC-FID and GC-TCD. The reactor temperature ranged from 400-550 °C and the methanol to ammonia ratio ranged from 0.5 to 2.0.

The catalysts were prepared by wet impregnation of the cobalt and tin precursors followed by calcination. They were characterized with powder X-ray diffractometry, scanning electron microscopy (SEM) with energy-dispersive X-ray spectrometry, temperature programmed reduction (TPR), infrared spectroscopy and Raman spectroscopy before and after reaction.

Results and Discussion

The results have shown that the preparative method of the catalysts has an impact on their characteristics, even though the precursors are the same. Accordingly, it can be seen that it does matter whether the cobalt and tin precursors are impregnated in one step or are impregnated sequentially, with a calcination in between and after. Fig. 1 shows the appearance of three different types of catalysts.

Figure 37: The appearance of the catalysts after (Left) co-impregnation, (Middle) impregnation with tin first, and (Right) impregnation with cobalt first.

The blue areas of the catalysts are expected to arise due to the formation of the blue compound $CoAl_2O_4$ [6]. The exact confirmation of this has proven difficult in the initial investigations, but findings from SEM, TPR and catalytic test suggest that there are differences between the blue and the black catalysts. Fig. 2 shows the SEM micrographs of the two right-most catalysts in Fig. 1.

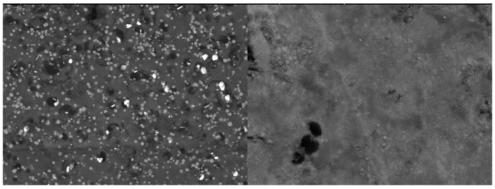

Figure *2*: The SEM micrographs of the catalysts after (Left) impregnation with tin first, and (Right) impregnation with cobalt first.

The micrographs show that the cobalt to the left is found as gray spheres of an oxide phase with tin as white agglomerates of SnO_2. To the right, the cobalt is distributed in a more continuous fashion.

The TPR characterization also yielded some useful information. Fig. 3 shows that a catalyst capable of forming $CoAl_2O_4$ (left) has an extra uptake of H_2 at 1000 °C, whereas a catalyst without this phase (Co-Sn/$MgAl_2O_4$) does not have that feature.

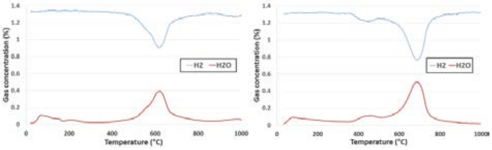

Figure 38: The results of the TPR experiments. The graphs show the water and hydrogen concentrations as functions of temperature for (Left) a Co-Sn/Al_2O_3 and (Right) a Co-Sn/$MgAl_2O_3$ catalyst.

The last interesting difference between the blue and the black catalysts is that the blue catalysts seem to produce both hydrogen cyanide and acetonitrile, whereas the black catalysts show no sign of hydrogen cyanide.

Conclusions

The experiments have shown that the way the Co-Sn/Al_2O_3 catalyst is prepared have an impact on the properties. Both the visual and catalytic differences are evidence hereof. The main conclusion so far is that the blacker catalysts do not seem to produce hydrogen cyanide.

Acknowledgements

This project utilizes the facilities at both Haldor Topsoe A/S and the Technical University of Denmark. Both institutions therefore play a big role and have a part in the funding.

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Catalytic Methanol Synthesis

(November 2017 – October 2020)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

Powering the world with scarce fossil resources is unstainable and changes toward renewables are required. Methanol produced locally from CO_2 at mild conditions can promote an energy efficient transition because it is a good energy carrier, but it requires development of methanol catalysts with highl activity at mild conditions. Through improved understanding of the active sites, methanol catalysts optimized to mild conditions can be developed and thereby promote carbon neutral energy at a competitive price.

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Abstract

Methanol synthesis is an important industrial process (80-90 million tons demand in 2018) and occurs by reacting H_2 and CO_2 over a $Cu/ZnO/Al_2O_3$ (CZnA) catalyst at 200-300°C and 50-100 bar [1]. However, the origin of CZnA's active sites remains highly debated. This project attempts to solve this debate by focusing on electron transfer between Cu and the support(s). Surface coverage of formate (θ_{HCOO}) on supported Cu catalysts after methanol synthesis at reaction conditions is quantified from desorbing CO_2. The methanol turn-over frequency (TOF: rate per Cu surface atom) is found to increase with θ_{HCOO} and decrease with the stretching frequency of CO (ν_{CO}) adsorbed on Cu, which supports the suggested electron transfer mechanism. This project is part of the Villum Center for the Science of Sustainable Fuels and Chemicals.

Introduction

Several studies report linear relations between the specific Cu surface area (m^2 Cu/g_{cat}) and the methanol rate ($g_{MeOH}/g_{cat}/h$) for supported Cu catalysts [2+3]. The rate to surface area ratio corresponds to the TOF, which also depends on the support. We hypothesize that electron transfer between Cu and the oxide(s) can account for the support effect on the methanol TOF.

Upon contact between an n-type semiconductor (such as the support) and a metal, the Fermi levels of the metal and support must align, which causes (high energy) support electrons near the interface to transfer to the metal resulting in the formation of a potential energy barrier. This barrier promotes an electron flow of conduction band electrons (from the support) towards the metal. Heating and/or reducing (in e.g. H_2) the support can remove oxygen atoms and generate oxygen vacancies (V_0) and free electrons, which may be trapped in V_0 or minimize its energy by moving to the metal [4].

HCOO is a key reaction intermediate for methanol synthesis and exhibits an electron-withdrawing nature [5+6]. Electron donation from the support through Cu to HCOO may therefore promote a high θ_{HCOO}. Consequently, the electron transfer mechanism predicts that Cu experiences support dependent electron donation or withdrawal, which regulates θ_{HCOO} with potential influence on the methanol TOF.

A linear relation between methanol TOF and θ_{HCOO} regardless of the support would indicate that electron flow can regulate the TOF through stabilizing θ_{HCOO}.

Infrared spectroscopy is applied to identify ν_{CO} with $\nu_{CO} < 2100\ cm^{-1}$ attributed to CO adsorption on metallic Cu and $\nu_{CO} > 2100\ cm^{-1}$ associated with oxidized Cu (e.g. Cu^+) [7]. Support induced electron donation to Cu can potentially be observed by shifts in ν_{CO}.

Specific Objectives

- Measure Cu surface area by N_2O-Reactive Frontal Chromatography (RFC) after H_2 reduction
- Determine methanol activity in $H_2/CO/CO_2$ = 68/29/3 at 250°C, 50 bar to determine TOF
- Quantify θ_{HCOO} by TPD after nitrogen quenching at methanol synthesis conditions
- Evaluate HCOO's decomposition temperature by diffusive reflectance IR spectroscopy (DRIFTS) to verify the quantitative method
- Determine ν_{CO} for CO adsorbed on Cu

Results and Discussion

Figure 1 outlines the quantitative procedure for obtaining θ_{HCOO} on Cu starting with reduction of

CuO to Cu using H_2. N_2O-RFC on pre-reduced catalysts determines the Cu surface area, which is applied together with results during methanol synthesis (250°C, 50 bar in $CO_2/CO/H_2$) to calculate the methanol TOF. After obtaining the methanol TOF, the catalyst is rapidly cooled by liquid N_2 quenching to fixate the configuration of surface species obtained at reaction conditions. After pressure release and He flush at cryogenic temperatures, the amount of evolved CO_2, H_2 and CO are measured by temperature programmed desorption (TPD).

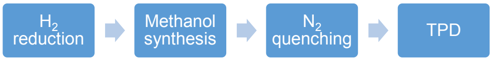

Figure 39: Protocol for quantifying θ_{HCOO} on Cu.

Because HCOO decomposes to H_2 and CO_2, they should in principle allow θ_{HCOO} to be quantified. However, significant H_2 desorption from the support necessitates, that the (apparent) θ_{HCOO} is quantified by integration of desorbed CO_2. Studies conducting similar IR experiments report Cu-HCOO decomposition at ~140°C identified by decreasing signals of $\nu_{Cu-HCOO}$ at 1600 cm^{-1} and 2850 cm^{-1} [5+8]. Figure 2 demonstrates a clear relation between the apparent θ_{HCOO} and the TOF.

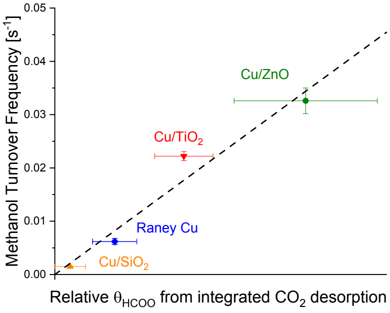

Figure 40: Methanol TOF (250°C, 50 bar in syngas) as function of apparent θ_{HCOO} obtained by integrating the CO_2 signal post methanol synthesis and N_2 quenching.

Validation of the quantitative method, where CO_2 and HCOO desorption are related, is provided by DRIFTS using a similar procedure as shown in Figure 1 but at milder conditions and replacing liquid N_2 with cold water. After formate synthesis at atmospheric pressure in $CO_2/CO/H_2$ at 100°C, the catalysts are cooled and flushed with He before heating the catalyst (TPD). Figure 3 shows the relative intensity (I/I_0) change of $\nu_{Cu-HCOO}$ (blue and red curves) together with evolved CO_2 signal (green curve) as function of temperature upon heating the partially HCOO covered surface. Concurrent evolution of CO_2 and HCOO decomposition ($\nu_{Cu-HCOO}$ decreases) in the temperature range characteristic for Cu-HCOO decomposition validates the applied method to quantify θ_{HCOO}.

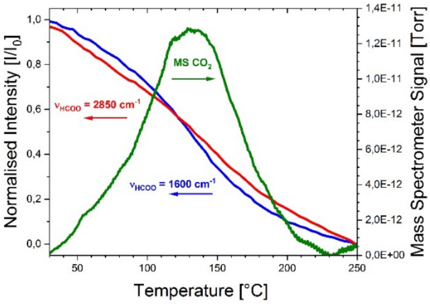

Figure 41: Combined MS and DRIFTS during TPD on a partially covered HCOO surface show CO_2 evolution as HCOO decomposes from Cu (decreasing $\nu_{Cu-HCOO}$) at ~140°C.

Conclusions

Quantification of θ_{HCOO} by CO_2 originating from decomposed HCOO correlates well with the TOF. In-situ IR results (not shown here) indicate that catalysts with redshifted ν_{CO} (w.r.t. pure Cu) yield high TOF. Donated support electrons to Cu can well explain both observations but the results provide no direct proof for the proposed electron transfer.

Future in-situ X-ray photoelectron spectroscopy (XPS) studies at ambient pressure are planned to deliver direct evidence for the suggested electron transfer mechanism.

Acknowledgements

We gratefully acknowledge the Villum Foundation V-SUSTAIN grant 9455 to the Villum Center for the Science of Sustainable Fuels and Chemicals.

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Novel Strategies for Control and Monitoring of Bio-Processes using Advanced Image-Analysis

(September 2018 - August 2021)

Contribution to the UN Sustainable Development Goals

This project contributes to the 12th UN sustainability development goal that aims for responsible consumption and production. In this work, particle processes in chemical and biochemical industry are targeted. Here, the aim is to reduce product waste due to product variations and to reduce the utility consumption of the processes. This is done using process systems engineering (PSE) approaches that utilize novel sensor techniques to assist in developing more sustainable particle processes.

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Abstract

This project aims to generate tools for monitoring, modelling and control of particle processes in chemical and biochemical process industries. Here, traditional chemical engineering modelling approaches are combined with machine learning methods, utilizing time-series data coming from traditional process sensors and on-line particle analysis. This offer novel, robust and flexible tools that have the potential of speeding up the development and design of new particle processes and for optimization and diagnosis of existing processes.

Introduction

Particle processes are used broadly in industry and are frequently used for removal of insolubles, product isolation, purification and polishing. These are also some of the most challenging processes to design and control due to their complex dynamics. In industry, this typically results in product variations that in many cases lead to significant product waste. Furthermore, many of these processes are today operated based on heuristics, which lead to a suboptimal operation, resulting in overconsumption of utilities.

However, in the last decade there has been significant developments within the field of non-invasive particle monitoring tools. It is now possible to obtain measurements of particle properties in real-time. By combining this new data with traditional process sensors, one can now obtain new insights in the process dynamics. This knowledge can subsequently be used to design, control and optimize these processes.

On-line particle analysis

In this project, dynamic image analysis is used for monitoring particle properties in real-time, and capture the particle process dynamics. Here, an on-line analysis equipment by ParticleTech [1] is used. The procedure of obtaining the particle properties can be seen in Figure 1.

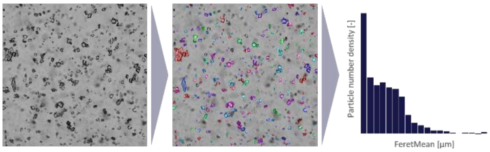

Figure 42: Particle analysis procedure using image analysis equipment by ParticleTech

Liquid suspensions of particles are here pumped from the process tank to a flow-cell inside a microscope unit, that captures images of the particles. Then, using a segmentation algorithm, the individual particles are identified. Finally, a number of features are extracted for individual particles, including particle size and shape.

Hybrid model framework

In this project, a modelling framework has been proposed [2,3], based on a hybrid modelling concept. The hybrid model structure allows for increased modelling flexibility towards the use of various process sensors, and requires only little prior process knowledge. At the same time, it ensures the predictions not to violate physical and chemical constraints.

Here, the hybrid model structure consists of a machine learning based soft-sensor, which is used for estimation of particle phenomena kinetics. The machine learning model inputs are here the measured process variables (x), the controlled process variables (y), and the time-derivative of the controlled variables (dy/dt). The outputs are the phenomena kinetic rates, which are fed to a mechanistic model including mass and population balances. The model structure of the hybrid approach can be seen in Figure 2.

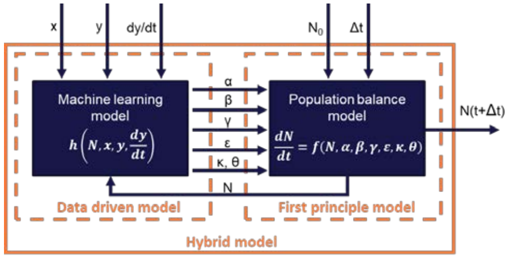

Figure 43: Hybrid model structure

The proposed hybrid model can be trained in real-time, which allows for updating the model continuously during process operation, utilizing the latest obtained sensor data.

Results

The hybrid modelling framework has been demonstrated on two crystallization case studies [2], including a laboratory scale food crystallization and an industrial scale pharmaceutical crystallization. In both cases, the modelling framework showed to capture the process dynamics with limited prior process knowledge and only few batch time-series data.

Future work

As future work, multiple promising use cases of the presented real-time updated hybrid particle model will be examined. This include screening for optimal process conditions, process scale-up/scale-down, process diagnostics, process optimization and process control.

As an example, in process control, one can use a model predictive control approach, where the hybrid model will be used to calculate the optimal control actions. At the same time, the hybrid model will continuously learn from the previous control actions, forming a platform for self-learning process control, that can refine the process control both intra-batch and inter-batch.

Furthermore, the loop can here work as a continued process verification, as recommended by the FDA [4] and can be operated fully automatic.

Conclusions

A hybrid modelling framework has been proposed, that allow for robust and flexible characterization of particle processes, using on-line particle analysis and traditional process sensors. The framework has been tested on two crystallization case studies, showing high prediction accuracy with even limited prior process knowledge and using only few batch time-series data.

The hybrid model allows for real-time training, opening up for multiple use cases, including screening for optimal process conditions, process scale-up/scale-down, process diagnostics, process optimization and process control.

Acknowledgements

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1. R. F. Nielsen, N. A. Kermani, L. C. Freiesleben, K. V. Gernaey, S. S. Mansouri, Novel strategies for predictive particle monitoring and control using advanced image analysis, 29th European Symposium on Computer Aided Process Engineering, volume 46 of Computer Aided Chemical Engineering, Elsevier, pp. 1435-1440, 2019
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Design of a silicone colorimetric sensor for antioxidant activity determination

(January 2017- December 2019)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

This project aims at developing a convenient and practical solid-state sensor for assessing the antioxidant activity of compounds and food samples. The design of the sensor reported here endorse the achievement of the Sustainable Development Goal 12 since it can be fabricated by means of an easy and cost-effective process and it requires limited amount of solvents to perform the test.

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Abstract

There is an increasing demand for the development of smart assays for the evaluation of antioxidant activity of compounds, food samples, and natural extracts, owing to the importance of antioxidants in counteracting oxidative damage in the human organism. This study reports the design of a solid-state and portable format of the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical test. The response of the colorimetric sensor is investigated qualitatively and quantitatively toward food samples and selected antioxidants of different nature, in order to determine their antioxidant activity.

Introduction

A disruption in the delicate balance that controls prooxidants and antioxidants in the human organism results in oxidative stress. Antioxidants play a key role in fighting the adverse effects related to oxidative stress, and, therefore, a lot of attention is focused on finding the most powerful antioxidant or the food with the highest antioxidant content.

Among the traditional *in vitro* antioxidant activity assays, the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical assay[1] is one of the most widely employed. The mechanism behind the DPPH test is based on a redox reaction associated with a colorimetric process. DPPH radicals show an intense purple color in solution (maximum absorption band at a wavelength of ~515 nm) and, when an antioxidant reduces the radicals, a change in color from purple to yellow is observed.

Optical colorimetric sensors provide a competitive alternative to solution-based analytical assays: they are facile, rapid, portable, and cost-effective.[2] Additionally, they allow for the naked eye and *in situ* detection of the results, and they enable a remarkable reduction in the volume of solvents employed to perform the test. In colorimetric sensors, the choice of the solid matrix used to immobilize the chemoresponsive dye is crucial.

Specific objectives

The objective of this study is to develop a colorimetric sensor for antioxidant activity determination by physically entrapping DPPH radicals into silicone elastomers.[3] Silicone elastomers were selected as a matrix owing to their favorable properties, such as versatility, easy processability, optical transparency, and flexibility. Reference antioxidants solubilized in different media and food samples are employed to inspect qualitatively and quantitatively the response of the sensor.

Results and discussion

DPPH radicals were immobilized in condensation cured silicone elastomers at a concentration of 0.03 wt%, which was found to be optimal. After curing, DPPH silicone is a free-standing elastomer (with a thickness of ~400 µm), and cylindrical samples can be cut and arranged to form a ready-to-use screening platform, as illustrated in Fig. 1. Ascorbic acid (vitamin C), α-tocopherol (vitamin E), and butylated hydroxytoluene (BHT) were chosen as reference antioxidants to investigate the response of the sensor. When drops of antioxidant solution are placed on the surface of the sensors, the antioxidants scavenge the DPPH radicals entrained in the silicone and induce a discoloration of the sensor from purple to yellow that can be evaluated visually. Vitamin E and BHT in isopropanol (IPA) caused an extent of discoloration correlated to their concentration in solution, in contrast to vitamin C in water (Fig. 1). Even though the sensor showed a positive response to vitamin C, two factors might compromise the efficiency of the sensor towards this antioxidant: the hydrophilic nature of vitamin C prevents its diffusion within the hydrophobic body of the elastomer and, additionally, water-based solutions are not capable of extracting DPPH radicals from the matrix.

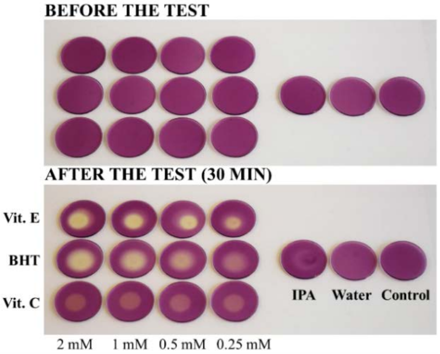

Figure 44: DPPH silicone sensors before and after dropwise application of solutions of vitamin E, vitamin C, and BHT at different concentrations.

Furthermore, DPPH silicone elastomers were coated on the bottom of the wells of a microplate in order to quantitatively measure the DPPH radical scavenging activity of the reference antioxidants through UV-Vis spectroscopy. The response curves of the sensor to antioxidant solutions were obtained by measuring changes in the absorbance at 514 nm over time (180 min). In Fig. 2, the radical quenching activities of BHT, vitamin E, and vitamin C are expressed by means of %DPPH scavenging effect [%DPPH scavenging effect= $(A_0-A_1)/A_0*100$, were A_0 corresponds to the initial absorbance of the sensor and A_1 corresponds to the absorbance of the sensor after being in contact with an antioxidant solution for 30 min].

As illustrated by the response curves in Fig. 3, microwell plates coated with DPPH silicone elastomers were also employed to measure the response curves of the sensor toward food and beverage samples without need of preliminary treatment, proving the practicality of the sensor. Moreover, stability studies showed a significant improvement in the stability of the silicone sensor compared to solid-state DPPH sensors previously reported.

Conclusions

In this study, the development of a solid-state, flexible, and portable format of the DPPH test is presented. The colorimetric sensor is fabricated by means of a simple process and can be used for a rapid qualitative assessment of antioxidant activity (yes/no test). When DPPH silicone is coated on the bottom of the wells of a microplate, antioxidant activity can be determined quantitatively by using UV-Vis spectroscopy. The results show a significant versatility and practicality of the sensor: it enables the analysis of unmodified food samples and both hydrophilic as well as hydrophobic antioxidant compounds, solubilized in different media.

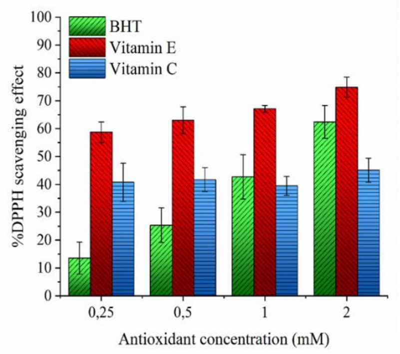

Figure 45: %DPPH scavenging effect of solutions of BHT, vitamin E, and vitamin C at different concentrations.

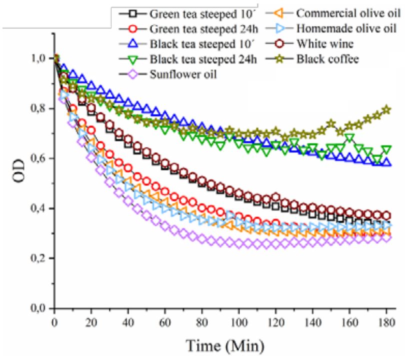

Figure 46: Time-dependent decay in absorbance of the sensor at 514 nm in response to unmodified food and beverage samples.

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Acknowledgements

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An *in silico* Tool for Crystallization Process Development

(January 2017- March 2020)

Contribution to the UN Sustainable Development Goals

Traditionally, pharmaceutical processes have been designed and developed based on a high number of experiments and considerable amount of resources in order to find an optimum operation. However, model based approaches can replace this high resource and time demanding conventional practice by cheaper and faster virtual experiments. This projects aims to support pharmaceutical crystallization process development and optimization studies by means of model-based approaches.

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Supervisor: Gürkan Sin, Jens Abildskov, Stuart M. Stocks

Abstract

This work presents an *in silico* tool that supports crystallization process development and optimization studies by means of mechanistic modeling, uncertainty identification, comprehensive sensitivity analysis and a quantified process risk assessment.

Introduction

Crystallization is still predominant separation and purification method during the recovery of solids from solutions especially in pharmaceutical industries [1]. The operating condition of a crystallization process is of critical importance because properties of a crystal product such as purity, size, shape distribution and polymorphic form depend strongly on the condition under which the crystallizer is operated [2, 3]. Moreover, these product properties affect the performance of the following downstream operations such as filtration and drying, and eventually efficacy of the product formulation. Traditionally, crystallization processes have been operated recipe-based in the pharmaceutical manufacture and the quality of the product has been determined by testing at the end of the process. Quality-by-testing (QbT) has often resulted in failed batches, which in return led to loss of profit, while the pressure of producing faster, cheaper and more efficiently has been increasing day by day [2, 4]. Process systems engineering methods and tools possess significant advantages over traditional methods; improving process understanding, speeding up process development and providing better control over process variables. Additionally, the FDA has promoted the usage of quality-by-design (QbD) approaches, integration of process analytical technology (PAT) tools into the process design and manufacturing as well as identification of uncertainties and quantification of process risk assessment [5, 6]. Therefore, the objective of this work is to develop an in silico tool for a pharmaceutical crystallization process to support design, optimization, control and uncertainty/sensitivity analysis for process risk assessment. The developed tool was used to explore an operational design space in order to guide the design using comprehensive sensitivity and uncertainty analysis as well as process risk assessment.

Methods

An *in silico* tool was developed for a batch cooling crystallization system. Crystallization of paracetamol from ethanol was chosen as a case study. The solubility and crystallization kinetic data of the mentioned solute-solvent system were taken from the literature [7, 8]. Related mass, energy and population balance equations are implemented and solved in MATLAB/Simulink environment. Several sources of uncertainties in process are identified and the effect of uncertain process parameters on the process output variability are quantified through uncertainty analysis. Sensitivity analysis is performed to investigate the design space of initial concentration, seed specification (mass, mean, sigma), cooling time and cooling profile. Finally, in order to assess the process risks due to variations in the operation design space (Figure 1), firstly the probabilities of not achieving the target yield and final mean crystal size are calculated. The risk is quantified by means of multiplying this likelihood of not achieving the target product specification with the consequence of this undesired event.

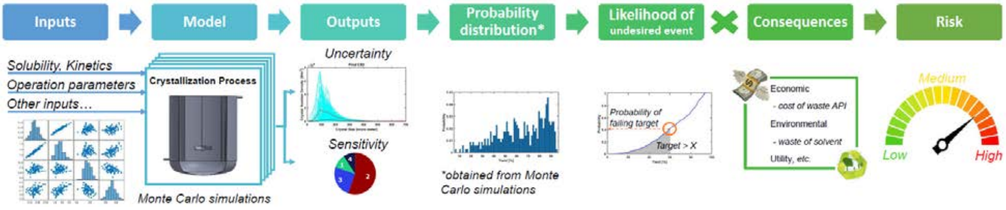

Figure 47: A schematic diagram of uncertainty and sensitivity analysis, and quantification of process risk.

Results and Discussion

A risk based approach requires understanding of how process factors affect the quality and performance of the product/process, which process variabilities have critical importance to achieve consistent product within desired quality requirements and therefore to quantify the risk of producing poor quality product. To this end, variations in the design space of operation parameters (*e.g.* initial concentration, cooling time, cooling time, seed mass, seed mean and std.) were identified and their effect on the process output is studied (Figure 2). Using the developed tool, a study on the quantification of process risks was performed. Sensitivity analysis results revealed process yield has strongly affected by cooling (batch) time, cooling profile and initial concentration, respectively. Seed specifications such as seed mean and mass as well as initial concentration plays the most important role in determining final mean crystal size obtained from the process.

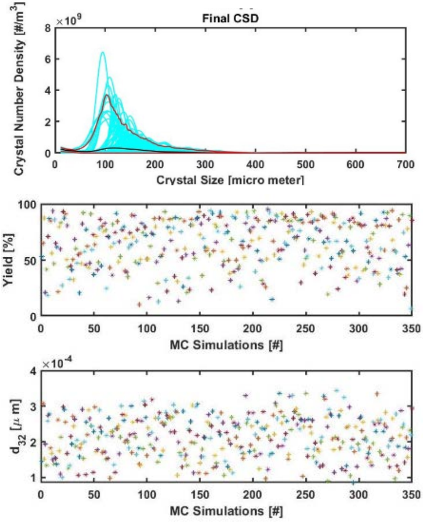

Figure 2: Total output uncertainty of batch cooling crystallization due to variations in operation design space.

Therefore, more effort should be given to optimize these parameters to get higher yield and optimized final mean crystal size. Finally, the economic risk of failing product target of final mean crystal size above 140 µm is calculated up to 151,700 $ per batch of 10,000 L suspension, when the API is a high value product (e.g. 500 $/kg).

Conclusions

In this study, we presented an *in silico* tool for a pharmaceutical crystallization process. We used uncertainty and sensitivity analysis to identify process variables and to quantify their effect on the process outcome for process risk assessment. As a case study, an application on the exploration of the operational design space was shown. Finally, the risk of failing process/product target due to variations in the operation design space was quantified. In conclusion, *in silico* tools provide an effective and cost-efficient platform to develop processes, investigate design spaces, to explore feasibility of different operation and control strategies and to quantify the process risks. Pharmaceutical industries can benefit from model based approaches through reduction of process failures, consistent batch-to-batch products and gaining acceleration to compete with challenging market driving forces.

Acknowledgement

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Pore to Core Scale Investigation of Gas Production Behavior & CO_2 Storage Potential in Gas Hydrate Reservoirs

(July 2018- June 2021)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

Large amount of methane-rich gas hydrate reservoirs, discovered in permafrost and deep ocean sediments, are seen as a source of cleaner energy and alternative to fossil fuels. Methane production from such deposits is currently being investigated using different production methods. Recently CO_2 rich gas injection into these reservoirs is proposed as a potential method to recover methane from hydrate deposits. This method is a carbon neutral method as it produces Methane and stores carbon dioxide in hydrates simultaneously without destabilizing the hydrates. This PhD project is focused to understand many unknown associated with this technique.

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Abstract

Understanding of Gas Hydrate formation, dissociation, and stability in geological sediments are essential for modeling these systems both concerning global warming and in schemes of CH_4 recovery and/or CO_2 storage. In this work, pore-scale (mm) visualization of CH_4 hydrate, formation, and dissociation in sedimentary rock in different temperature range is carried out using the micromodel and image analysis. The primary purpose of the research work is to evaluate CH_4 hydrate dissociation kinetics containing different hydrate saturations and at a temperature above and below the Ice point and further compare the self-preservation characteristics. Pore level visualization is carried out in transparent, etched, micromodel of sedimentary pores of a 2D thin section of the actual sandstone rock.

Introduction

Gas hydrates are ice-like crystal compounds formed when water and gas come together at high-pressure and low-temperature conditions. Many gases are known to form a hydrate, but the most exciting gases for research purposes are methane (CH_4) and carbon dioxide (CO_2). Methane gas is naturally found in hydrate form in colder regions, such as the permafrost region in Alaska, Siberia, and deep ocean sediments, as in the South China Sea, Gulf of Mexico, and Japan Sea.

These methane hydrate deposits are considered a potential source of gas recovery in the coming years, and my research is focused on recovering methane gas by injecting CO_2 gas that replaces CH_4 and allows CO_2 storage in the same place. Hydrate formation in sediments is a complex phenomenon, and it is important to understand the pore-scale mechanisms to exploit it on a large scale. Micromodel-based, pore-scale experiments are very useful experimental tools to observe the fluid flow behavior within pore space. Micromodel is also known as microfluidics, includes microchip mimicking rock pore structure at the micrometer scale. With the help of pore-scale visualization, we could understand the hydrate formation and dissociation behavior and correlate the microscale experiments with core-scale findings. Micromodel chips will also help to visualize the effect of different pore sizes and the effect of salinity on formation and dissociation mechanisms. In general, flow within micromodel is laminar, hence transportation of liquid is predictable and easily observable due to the transparent nature of the microchip. Experiments are performed in a controlled manner using controlled flow rates and pressure.

There have been few attempts to use a micromodel setup to study gas hydrates in pore spaces. The first evidence of hydrate studies using micromodel is found in the paper by Tohidi et al. (2001)[1]. In this research, glass micromodel is used to visualize the hydrate formation in the presence of hydrate promoter tetrahydrofuran, free methane gas, and free carbon dioxide. Another notable research by Katsuki et al. (2007)[2] has studied the effect of the system subcooling effect on the methane hydrate growth using glass micromodel. Conversion of dendritic hydrate crystals into particulate hydrate systems was observed at the higher subcooling (greater than 12K). In one of the recent papers by Hauge et al. (2016)[3], the formation of methane and CO2 hydrate in high-pressure silicon micromodel was studied. They have visualized that the hydrate growth pattern depends on fluid connectivity and local fluid distribution.

Specific Objectives

the primary purpose of this research is to understand gas hydrate formation and dissociation in the porous medium. My research involves pore level (micrometer) to core-scale (centimeter) experiments to understand methane gas hydrate formation and dissociation behavior. I also study the influence of different parameters, including initial water/gas saturation and sediment properties, on methane recovery and CO_2 storage.

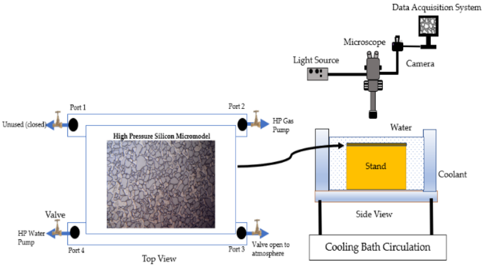

Figure 1: Micromodel chip saturated with water and gas (left) and experimental setup (right)

Methodology

Pore Scale Experiment

In this study, a silicon-based micromodel is used for hydrate formation and dissociation visualization. Micromodel is built by a glass plate anodically bonded with a silicon wafer. Anodic bonding procedure leads to water wet micromodel. The water wet nature of solid grain induces the curve interface between water and gas and easy to differentiate between different fluid phases. The model consists of average pore diameter of 100 um and a constant vertical height of 25 um. Pore shape and size are based on thin section analysis of the sandstone. This reproduction of actual pore bodies, pore neck, and coordination number makes the model suitable for the fluid flow and phase equilibrium phenomenon. Micromodel based images are acquired, and segmented images are generated to calculate the two-dimensional fluid saturation.

Core Scale Experiment

For the core scale experiment, bentheimer sandstone will be saturated with a brine made of different salinity. For saturation, spontaneous imbibition will be selected. Once methane hydrate is formed in brine saturated cores, CO_2 abundant gas will be injected to study the methane recovery by CO_2 injection.

Initial Results

Understanding of initial hydrate saturation is very critical of the selection of correct production technique. Hydrate saturation and water saturation plays a crucial role during the dissociation in the permafrost region. Very high and very low hydrate saturation both show a negative effect on the rate of hydrate dissociation due to the presence of a high self-preservation effect. (Figure 2)

Due to different hydrate melting mechanisms, hydrate dissociation rates and patterns are different for hydrate shells and hydrate crystals. When pressure front arrives at the pore space, hydrate shells start to dissociate from the center of the pore to corner due to differences in thickness while hydrate crystals melt uniform, releasing the free gas which further dissociates neighbor hydrates. Gas only began to mobilize in the former case, when hydrate shells are completely melted while it is not the case with hydrate crystals.

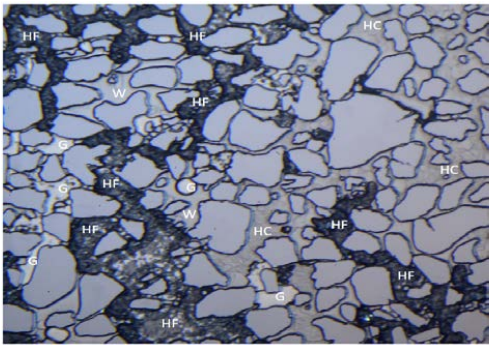

Figure 2: Example of High gas hydrate saturation in micromodel. HF refers to hydrate film, HC refers to hydrate crystals, G refers to free gas, and W refers to water.

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Ecological Control Strategies for Biobutanol Production

(January 2018- December 2020)

Contribution to the UN Sustainable Development Goals

For a smoother transition towards a bio-based society, no longer dependent on current liquid fossil fuels, sustainable alternatives to energy sources like gasoline and diesel need to be implemented. Due to their similarities, butanol can already today be used as direct replacement for gasoline. In this project we aim at producing butanol from butyrate, a low-value substrate and often disposed of in biotech processes, contributing therefore for the recovery of waste products into added-value commodities.

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Abstract

For a smoother transition towards a bio-based society, no longer dependent on current liquid fossil fuels, sustainable alternatives to energy sources like gasoline and diesel need to be implemented. Due to their similarities, butanol can already today be used as direct replacement for gasoline. Due to their microbial diversity, mixed microbial cultures (MMC) can overcome the limitations of pure cultures and potentially become the predominant bio-based production platform for biobutanol. Butanol can be produced using only butyrate and hydrogen (H_2), common intermediates during the decomposition of organic residues, as is the case for industrial waste streams. By consuming a cheap feedstock alternative that avoids competition with food production, we contribute to a more circular and sustainable fuel bioeconomy.

Introduction

Accounting for nearly 65% of the world´s consumption [1], liquid fossil fuels are the major target for renewable and sustainable research. The search for renewable liquid fuels capable of replacing e.g. gasoline and diesel has in many cases focused on biorefinery approaches. Here, different generations of renewable feedstocks have been used but recently, in an effort to go even further, many resources that were once seen as waste are now the focus of valorization and recovery [2].

Bioethanol and biobutanol are the two top contenders for liquid fossil fuel replacement. But of the two, biobutanol is a much more interesting biofuel, with a higher energy density, can be blended with gasoline to any ratio without engine modification, low solubility in water, and higher boiling and flash point making it safer than bioethanol [3].

The most common process for biobutanol production is the Acetone-Butanol-Ethanol (ABE) fermentation by anaerobic bacteria, mostly belonging to the *Clostridia* family. Although pure cultures of *Clostridium* can achieve high yields, they have strict glucose requirements. In this context, mixed biotechnology is seen as a promising solution over pure strain culture due to its many advantages: non-sterile conditions, mixed and/or waste substrates, ecological selection, and continuous operation processes [4, 5].

Specific Objectives

The focus of the project is to enrich butanol-producing microorganisms through directed ecological selection in a continuously stirred tank reactor, starting from non-defined microbial communities fed on butyrate and hydrogen. By engineering the environment rather than the organism, we move towards the use of low-value feedstock for the production of a valuable chemical such as butanol, as opposed to the use of higher value substrates e.g. glucose, contributing to the progress of circular bioeconomy.

Results and Discussion

To ensure process consistency, batch fermentations in Schott bottles closed with butyl rubber stoppers were first conducted to determine possible limitations of the selected MMCs. It was found that anaerobic butyrate conversion was selectively inhibited under the chosen operational conditions (pH 5.5 and p_{H_2} of 1.5 bar), and production of butanol from butyrate was favored

(Figure 1). Other studies have also shown this to occur [6].

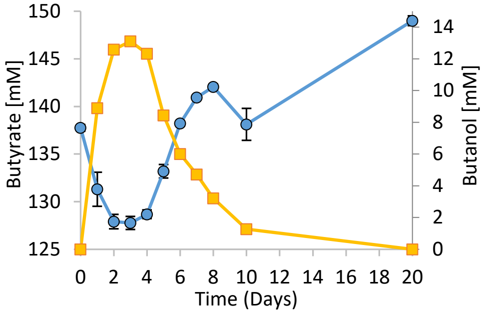

Figure 48. Butyrate (blue) and butanol (yellow) profiles in Schott bottles.

Interestingly, after 3 days of fermentation, butanol production stopped and even reverted(Figure 1). Pathway reversibility is likely to occur for reactions that proceed very close to thermodynamic equilibrium.

If conditions are favoring, the reverse reaction to butanol production from butyrate is possible. For that, the pH would have to be higher than the initial pH set for each experiment (pH 5.5). Due to the nature of the experiment, pH control when using Schott bottles is not much feasible, and as such when butyrate was consumed it increased the pH of the fermentation to close to pH 6.5 leading to worse conditions for butanol formation and better conditions for butanol conversion into butyrate.

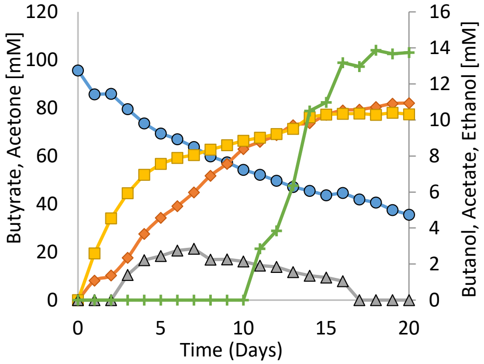

Figure 49. Butyrate (blue), butanol (yellow), acetone (orange), acetate (grey) and ethanol (green) profiles for butyrate conversion in a bioreactor system.

Throughout the fermentations, production of acetate was also detected, up to concentrations of 120 mM. This could be the result of anaerobic butyrate conversion, but at the present hydrogen partial pressure this reaction is inhibited. Upon further investigation, it was detected that a high concentration of bicarbonate was present in the initial inoculum used. Acetate production from bicarbonate, also known as homoacetogenesis, is favoured at hydrogen partial pressures above 5 mbar [7] and could explain the production detected.

Moving forwards to a system were pH control is possible at the desired set point, first butanol production is still observed and second plenty of other secondary metabolites are produced (Figure 2).

Conclusions

Butanol production from butyrate and hydrogen is feasible under the set of conditions initially hypothesized. pH control showed to be of essence, and when scaling up the current system to bioreactors (> 2L) this will became more feasible and expected to help achieve better yields. The butanol concentrations obtained in this work were about three times larger than previously reported [8], hinting at future applications of MMC for continuous butanol production from waste streams.

Acknowledgements

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Acknowledgements also to Farah Ali El-Zouheiri (MsC) for her contribution in the GREENLOGIC project.

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Optimization of geopolymer cement technologies

(April 2019- April 2022)

13 CLIMATE ACTION

Contribution to the UN Sustainable Development Goals

The production of Ordinary Portland cement production constitutes an 8% of the global CO_2 emissions. Therefore, there is a need for developing low CO_2 cement technologies. This study will focus on replacing the clinker with geopolymers or alkali activated materials, as they seem to largely reduce the CO_2 emissions, consume less energy, can reuse waste material and have comparable performance to the Ordinary Portland cement.

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Abstract

High emissions in cement industry derive from burning the limestone which accounts for more than 50% [1] of all the cement production emissions. Geopolymer cements do not burn limestone and can perform as well or better than Ordinary Portland cement, so their use can greatly reduce the CO_2 emissions. However, geopolymer production technologies have still some barriers to overcome such as the availability of raw materials. In this study, clays are studied as a potential aluminosilicate source for geopolymers.

Introduction

Concrete is the second most used commodity after water and is produced in volumes above 10 billion tonnes per year worldwide [2]. The binder used in modern concrete is called Ordinary Portland cement (OPC) and its production emits a large amount of CO_2 (~8% of global CO_2 emissions [3]). More than 50% of the CO_2 emitted in the cement production derives from the limestone calcination to calcium oxide and from the fossil fuel combustion used in the calciner and kiln. In addition, there is a high energy consumption deriving from heating the kilns, grinding the clinker and driving the mills.

The international scientific community has addressed the environmental issues associated with the cement production and there is a global environmental goal to reduce their associated CO_2 emissions. Consequently, new alternatives have been considered such as energy efficiency measures, CO_2 capture, alternative fuels or replacement of the clinker with alternative cement types (decarbonisation of the process) [4].

This PhD study will focus on replacing the clinker with geopolymers or alkali activated materials, as they seem to largely reduce the CO_2 emissions, consume less energy, can reuse waste material and have comparable performance to Ordinary Portland cement (OPC) [5].

The geopolymers can substitute the clinker by the reaction of an aluminosilicate material (calcined clay, fly ash, slag, red mug or rice husk ash) and a strong base such as sodium or potassium hydroxide and water [6].

Geopolymers have already been used in the industry as fire-proof materials, heat-resistant composites and ceramics. It has only been in the last few decades that has gain more attention as low CO_2 cement [7]. However, there are still some challenges associated to their commercialization. Some of them are related to the fact that the literature published is based on locally available raw materials, so it derives in variable compositions and properties of the resultant geopolymer. There are also some issues related to the use of aluminosilicate and alkaline materials, such as alkali efflorescence, aggregates formed in the alkali-silica reaction and leaching of toxic materials if industrial wastes are used as raw material.

For overcoming these barriers, this PhD study will intend to select raw materials (aluminosilicate and alkali) available worldwide and will formulate appropriate mix proportions, so that the reaction occurs optimally.

Specific objectives

The aim of this study can be summarized in the following bullet points:

- Reduce the CO_2 emissions derived from the cement production technologies using geopolymers
- Test the quality of geopolymers produced with selected raw materials aiming similar performance to Ordinary Portland cement

- Provide technology and process design recommendations for an efficient geopolymer production including an economic and environmental assessment

Selection of raw materials

The geopolymerisation reaction occurs between an aluminosilicate and alkaline activator in the presence of water.

As aluminosilicate source, calcined clays are selected due to their abundance all over the world. Figure 1 shows three types of clays soil distribution (kaolinite, illite and smectite).

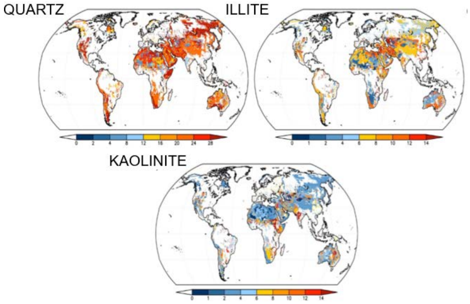

Figure 50: Global distribution of the effective mineral content in soil in percentages for quartz, illite and kaolinite [8].

For the alkali activator, a combination of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) are chosen for this study. They are the most common alkali activators used in geopolymers and they can dissolve better the aluminosilicates when compared to other activators such as carbonates and sulfates [9].

Planned investigations

An optimal mix design of the raw materials is going to be investigated. The aim is to produce a Metakaolin geopolymer concrete with a minimum compressive strength of 42.5 MPa and compare it to an ordinary reference cement CEM I 42.5 N. Moreover, this study attempts to use ambient curing temperature (21 ℃) and the lowest concentration of alkaline activators possible, as long as the targeted compressive strength is ensured.

The variables that will be investigated are the ratios of *Metakaolin-to-water*, *Na_2SiO_3-to-NaOH* and *NaOH molarity*.

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Recycling of waste from coating industry

(April 2019-April 2022)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Waste prevention, minimization, reuse and recycling are important measures to ensure sustainable consumption and production. Blast cleaning, as an important operation for ship repair and maintenance, generates large quantities of solid waste, which are usually disposed of in landfill at present. Therefore, it is important to work on the recycling of ship blasting waste to reduce land resources occupation by landfill disposal and to facilitate an efficient and sustainable use of natural resources.

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Abstract

Dry abrasive blasting with minerals, slags, or metallic grits is conventionally used for coating removal prior to repainting in shipyards. As a result, a large quantity of dust and solid waste is produced, which is usually landfilled at present. Alternative treatment methods, such as thermal treatment, solidification/stabilization/leaching technologies, physical separation, or reutilization as construction materials have been explored in literature. But most of these methods are still challenged by the high process cost and/or low product value. Recently, abrasive media blasting is being gradually replaced by ultra-high pressure (UHP) water blasting to reduce waste generation and dust emissions. Nevertheless, treatment of solid waste from UHP water blasting has almost not been reported in open literature. To minimize the environmental impact and to increase the value of shipyard blasting waste, this Ph.D. project is aimed to develop a novel recycling method to treat ship blasting waste, especially paint waste, and to optimize the process.

Introduction

Paint coatings, such as anticorrosive and antifouling coatings, are used to protect marine vessels. However, during marine transportation, coating degradation and rusting of the vessel surfaces occur as a result of operation or other mechanical impacts. In order to keep an optimal operation condition, a ship is docked for repair and maintenance on a regular basis[1]. In the ship repair process, foreign matters such as oil, grease, salts, attached marine organisms and slime are firstly washed down by high pressure water, followed by the removal of rust and old paint via spot or full blast cleaning[2]. Conventionally, blast cleaning is mainly accomplished by blasting the surface with an abrasive media such as minerals, slags, metallic grit or shot, etc. During this process, a large quantity of dust and abrasive blast media (ABM) waste (see Figure 1) is produced, which mainly contains original abrasive media, paint chips, and rust. Recently, abrasive media blasting is being gradually replaced by ultra-high pressure (UHP) water blasting to reduce waste generation and dust emissions. However, a considerable amount of slurry waste, which contains wastewater, paint chips, and rust, is still generated. The management of blasting waste produced in shipyards is of both environmental and economic importance.

Figure 1 Dry abrasive blasting activity (left) and "mountains" of ABM waste (right) in shipyard

At present, the ABM waste produced in shipyards is usually landfilled. However, landfilling is challenged by the shortage of landfill sites, rising cost, and more stringent environmental regulations. Up to date, alternative methods for the treatment of ABM waste have been explored, as summarized below:

- Thermal treatment methods, including incineration, pyrolysis and gasification, have been applied to destruct the toxic organic compounds in ABM waste, and to produce a solid residue that can be used for building materials, cover soil at a landfill site, raw materials for ceramic manufacture, or activate-carbon like materials[3, 4].

- Solidification/Stabilization/Leaching methods have been used to reduce the amount of leachable toxic species in ABM waste. This is achieved either by solidification and/or stabilization using chemical additives such as cement and lime[5, 6], or by solvent leaching followed by chemical precipitation[7].
- Physical separation methods, such as size classification, flotation, magnetic separation, gravity separation, electrostatic separation etc., have been used to separate the waste into hazardous and non-hazardous fractions, and thereby decreasing the amount of waste to be landfilled[8, 9].
- Production of construction materials, such as cement, concrete, mortar, bricks, etc.[10-12].

Most of the methods described above have been investigated only in laboratory- or pilot-scale, mainly due to the challenges in the high process cost and/or low product value. In addition, compared to AMB waste, waste from nonabrasive blasting (e.g., UHP water blasting) tends to be predominantly paint chips, which are usually hazardous. Besides landfill disposal, the alternative treatment of such solid paint waste has almost not been reported in open literature.

Objectives

The main objective of this project is to develop a novel recycling method to treat ship blasting waste, especially paint waste. Detailed information on the fate of major components in the recycling process will be provided and the process parameters will be optimized. Additionally, the application of the recycled product and its reuse feasibility will be investigated.

Acknowledgements

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Cyclic Distillation Technology

(December 2018 - November 2021)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Distillation is an important separation process that is used in chemical and biochemical industry all over the world. It is also a process that often takes place in huge columns with many trays and have significant energy requirements. Cyclic distillation is a process intensification that can reduce the energy consumption and number of trays compared to a conventional distillation. This way cyclic distillation can then be a cheaper and more environmentally friendly alternative to conventional distillation.

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Abstract

Cyclic distillation has been shown to be a promising process intensification that have higher tray efficiency compared to conventional distillation. It is a rather old technology, from the early 1960’s, but there is still a substantial need for developing and maturing the theory before the process can be a viable alternative to conventional distillation in industry.

Introduction

Cyclic operation of a distillation process is a process intensifying alternative to a conventional distillation process. Unlike the conventional distillation with counter-current liquid and vapor flows, the phase flows in cyclic distillation are separated in two periods: one where the liquid holdups are kept stationary on the stages and one, where the liquid holdup on each stage is drained to the stage immediately below. The two periods are called the vapor flow period (VFP) and the liquid flow period (LFP), respectively. After the liquid flow period a new cycle, beginning with a vapor flow period, is started.

There are two methods of draining the liquid holdups on the trays: simultaneous and sequential draining, each of which requires a special tray design [2]. For the simultaneous draining, the vapor flow is interrupted after the vapor flow period in order to allow all the trays to drain to the tray immediately below all at once, whereas for the sequential draining, the trays are drained one by one starting from the bottom. By draining with the sequential method, it is not necessary to interrupt the vapor flow.

By separating the phase flows, as described above, increased tray efficiency and throughput compared to conventional distillation processes can be achieved, as first shown by Cannon in 1961 [1]. With higher tray efficiencies, fewer trays are necessary and thus smaller columns can be made. Furthermore, a cyclic distillation process can reduce the energy requirements compared to a conventional distillation [2], thus making the distillation process more environmentally friendly by both reducing the size and energy for the column.

Cyclic distillation is, despite being almost 60 years old, still a technology that is under development. The current state-of-the-art model by Pătruţ et al. [3] is rather limited by only accounting for the mass transfer and single saturated liquid feed. Furthermore, most of the available models for cyclic distillation are only for the simultaneous draining [2].

Specific Objectives

The objective of this project is to further develop the necessary theory and models to properly describe a cyclic distillation process with either simultaneous or sequential draining. With more advanced models that includes considerations of energy transfer, it would be possible to simulate a distillation process in more details, for example for column designs or process control studies. More detailed models would also make the process more interesting as an alternative to conventional distillation for industrial use.

Results and Discussion

A new model for cyclic distillation with simultaneous draining has been developed based on the current state-of-the-art model [3]. The proposed model is a general stage model that can account for heat and mass transfer in LFP and VFP and allows for feed and side draws at any stage. Furthermore, an additional energy term is included that allows the model to easily account for heat of mixing, heat of reaction or heat integration on any tray if necessary. Figure 1 shows the stage model with inlets and outlets in VFP and LFP for simultaneous draining.

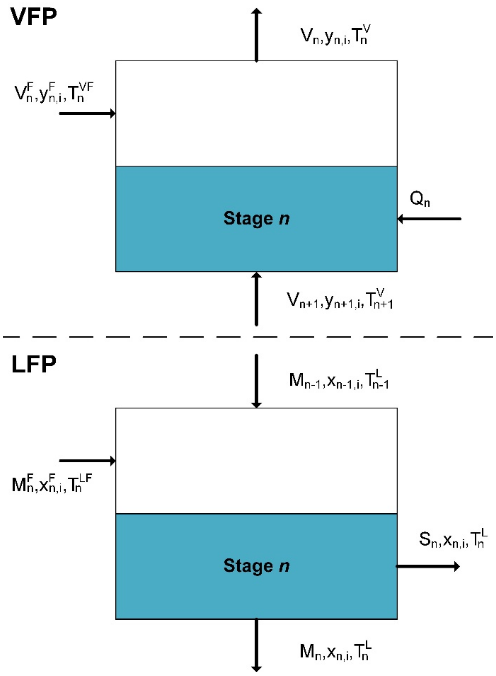

Figure 1: Stage in cyclic distillation with simultaneous draining during VFP (top) and LFP (bottom).

With this new stage model, it is possible to simulate the changes in the liquid holdups as well as the temperatures over time. This also allows to investigate feed that is not necessarily saturated liquid, but could for example also be vapor or subcooled liquid.

The proposed model that includes the energy transfer also allows for a more detailed design, more comprehensive process control studies and overall more realistic simulations. As mentioned previously, reactions can be readily implemented in the model by introducing a reacted/produced term in the mass balances and set Q_n as the reaction enthalpy in the energy balances.

So far, only a model for the simultaneous drained cyclic distillation has been made and no detailed models for sequential draining is available in literature. It would therefore be interesting to set up an equivalent model for sequential draining. This would make it possible to simulate either draining method and compare the two models.

Comparisons between the two draining methods have been made, but only with simple models for an ammonia three staged stripping case with linear equilibrium. These comparisons showed the duration of the VFP and the LFP are very important when designing a cyclic distillation. The longer VFP, where all stages undergo mass transfer between vapor and liquid, the higher degree of separation. However, a long VFP also means low throughput. A benefit in the sequential draining could be that during LFP it is only the draining and the filling trays, where no mass transfer between vapor and liquid occurs. On the other hand, the sequential draining of all trays is more time consuming, especially when having many trays, since the draining is done one tray at a time. In order to be able to investigate the sequential draining method further, more detailed models for this is necessary. With more detailed models for sequential draining, it would also be possible to compare the two draining methods for more complex cases, such as reactive distillation.

Conclusions

Cyclic distillation is a promising alternative to conventional distillation, with higher tray efficiencies that can lead to reduced energy consumption and smaller distillation columns.

It is still an emerging technology, which needs to be further developed. A general stage model has been developed for simultaneous drained cyclic distillation that includes both the mass and energy transfer. However, there is still a need for an equivalent model for sequential draining.

Comparisons between the simultaneous and sequential draining methods have been carried, but only for a simple case.

There is still many different aspects of cyclic distillation that need to be investigated, such as reactive distillation, comprehensive design algorithms and process control configurations.

Acknowledgements

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Development of dynamic CFD-based compartment models to study gradients in fed-batch fermentation processes

(March 2017- June 2020)

Contribution to the UN Sustainable Development Goals

The core of industrial biotechnology lies on fermentation processes, which are widely used for the sustainable production of a vast array of products, such as enzymes and bulk chemicals. Industrial fermentation processes are normally run at large scales with volumes ranging up to hundreds of cubic meters. Therefore, the formation of inhomogeneous conditions that can affect microbial physiology is likely to occur. It is just by studying the occurrence and magnitude of these gradients that we can understand and prevent them. This can ultimately lead to higher productivity and to more viable and sustainable processes.

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Abstract

Modelling of gradients in fermentation processes is a good approach to understand their impact and further prevent them. To this end, computational fluid dynamics (CFD) simulations are normally performed, since they give a precise description of the fermentation environment. Their combination with microbial kinetic models leads ultimately to the assessment of the impact of gradients on fermentation processes. Nevertheless, CFD simulations are computationally expensive, especially combined with kinetic models, and they are only useful to determine a fixed-volume snapshot of the fermentation. The development and use of dynamic CFD-based compartment models (CFD/CM) is therefore promising for the flexible assessment of variable-volume fed-batch fermentation processes.

Introduction

It is well known that gradients in reactor conditions occur when increasing scale in fermentation processes, due limitations in the mixing and the mass transfer capabilities of the systems. These heterogeneities can lead to the occurrence of the so-called scale-up issues, which yield to reduced productivity, product titer and quality [1,2]. The reason is that the organism does not perform at the operational settings but at suboptimal conditions, since cell performance strongly depends on the environment. Thus, understanding the cell mechanisms consequence of the presence of gradients is needed if we want to improve the process and its scale-up.

Modelling of gradients is a good approach to understand them. The use of computational fluid dynamics (CFD) simulations has been the core of *in silico* investigations, since they allow a trustworthy description of the flow field and of the interactions between liquid/gas phases in aerobic processes. Furthermore, their combination with microbial kinetic models ultimately leads to the assessment of the physiological repercussions of gradients on fermentation processes. The main disadvantage of using CFD simulations lies with their large computational demand which results in long simulation times (from several weeks to months), especially when microbial kinetics are included. This inconvenience has been successfully overcome by simplifying the CFD results into compartment models (CM). These CFD-based compartment models (CFD/CM) consist of a network of ideally mixed volumes (compartments). The flows between these compartments are such that the overall network can represent the flow behavior of the CFD results. CFD/CM have already shown great potential when capturing the dynamics of the CFD results with negligible simulation time. However, the bottleneck for their full exploitation is the fact that they can only be used for fixed-volume processes, i.e. to dynamically evaluate batch processes or to check snapshots of both constant and variable-volume processes.

In this contribution, a methodology to evaluate the impact of gradients on variable-volume fermentation processes, such as state-of-the-art industrial fed-batch processes, will be presented and applied to a large-scale (90 m^3) case study.

Methodology

To develop dynamic CFD-based compartment models for aerobic fed-batch processes, it is firstly needed to perform gas-liquid CFD simulations at different working volumes (Figure 1).

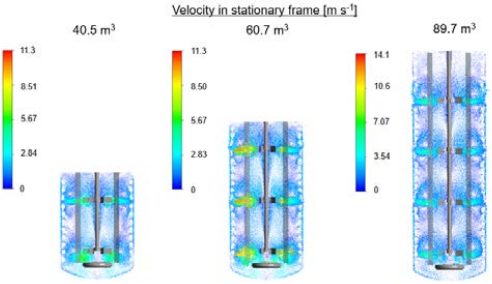

Figure 51: Two-phase CFD simulation results portraying the velocity in stationary frame for three different reactor volumes (40.5, 60.7 and 89.7 m^3). The system is agitated with 2, 3 and 4 Rushton turbine disk impellers, respectively.

The second step is to compartmentalize the CFD results based on the velocity profiles and extract the compartment flows and the OTR parameters. This is done following an automated compartmentalization approach [3] (Figure 2).

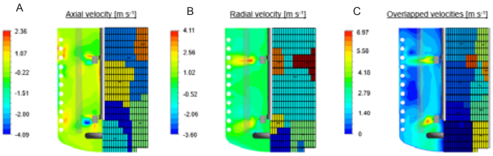

Figure 2: On the right, CFD results. On the left, CFD-based compartment map. This has been done for the axial velocity (A), radial velocity (B) and overlapped velocities (C) of the 40.5 m^3 simulation.

Finally, it is needed to re-compartmentalize the CFD results when the compartment map is significantly different. A volume change of 10% has been chosen accordingly to update the compartment map. The collection of compartment maps is shown in Figure 3.

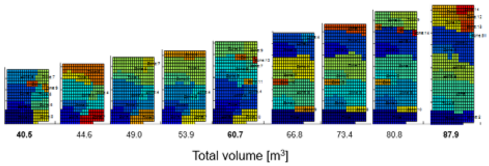

Figure 3: CFD-based compartment maps for volumes ranging from 40.5 to 89.7 m^3.

From the CFD results, correlations for the gas hold-up, the k_La and the power input per volume with the total volume can be established. The gas hold-up correlation can be used to linearly interpolate the volumes between compartment maps before they are updated. On top of that, the volume change due to the additions of feed rate is also taken into account. The correlation with the power input per volume will be used to establish any change of the flows between compartments. Finally, the change of the k_La over the fermentation will be provided to the model to calculate the oxygen uptake rate.

Results

The dynamic compartment model has been extended with a kinetic model for the bacterium *Bacillus licheniformis*, widely used in industry for the production of proteases and amylases. Its process is an aerobic fed-batch fermentation, meaning that gradients of glucose and dissolved oxygen can potentially occur. An example of the distribution of process variables is depicted in Figure 4.

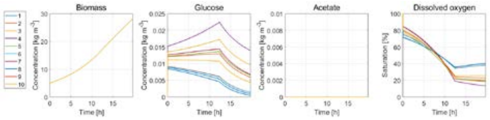

Figure 4: Distribution of process variables in phase 1 (40.5 to 44.6 m^3) in 10 different compartments.

Conclusion

In this work, a dynamic CFD-based compartment model for aerobic fed-batch operation has been developed and tested with a microbial kinetic model for *B. licheniformis*. The outcome is the prediction of different values for the process variables in different compartments. Future work will involve exploiting this approach to assess the impact of gradients on microbial physiology and on fermentation process performance.

Acknowledgments

Special thanks to Tannaz Tajsoleiman for all knowledge and advice provided regarding compartmentalization. This project receives financial support from the Technical University of Denmark and Novozymes A/S.

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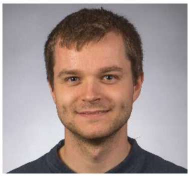
Cracking of Sugars for Production of Chemicals

(November 2017- November 2020)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Responsible production and consumption of chemical products are vital elements in sustainable development, as the current production is heavily based on non-renewable fossil resources. Platform molecules are important in the chemical industry as they are products that can be produced efficiently and used in several other chemical conversions and applications. For a chemical industry based on renewable feedstocks, new platform molecules will be needed. In this project, sugars are investigated for their conversion to glycolaldehyde, a potential platform molecule, used for further conversion to useful products such as ethylene glycol.



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Abstract

In this project, a process utilizing spraying of a liquid sugar solution, into a fluidized bed reactor is investigated. When an aqueous solution of glucose is used, this “sugar cracking” process can selectively produce oxygenates, with the main product being glycolaldehyde, a C2-oxygenate with yields as high as 74 wt%. Glycolaldehyde can be used for further sustainable production of useful products such as ethylene glycol. The project work is focused on obtaining a mechanistic understanding of the sugar cracking process to reduce the risk during process scale-up.

Introduction

Biomass represents the most readily available source of renewable carbon and is considered a promising feedstock for sustainable production of chemicals and fuels. While other renewable resources such as solar, water and wind can be used to produce heat and power, biomass can potentially be used for production of chemicals as well as renewable liquid, solid and gaseous fuels.

Production of chemicals from biomass, particularly the conversion of sugars to value-added chemicals are of interest. Hexoses are carbohydrates with six carbon atoms, and they are the most abundant monosaccharides in nature, among which fructose and glucose are the most economical and suitable feedstocks for chemical production [1]. Glucose is produced from hydrolysis of starch, and fructose can be produced from base catalyzed isomerization of glucose or by hydrolysis of inulin or sucrose [2].

It has previously been shown that fast pyrolysis can be used to convert glucose to glycolaldehyde in high yields (>50 wt%) along with other chemicals by spraying an aqueous solution of glucose into a fluidized bed operated at 500 – 600 °C [3]. This method of sugar conversion is called “sugar cracking”.

Glycolaldehyde can be hydrogenated in a second step to produce ethylene glycol (EG), which is a large commodity chemical with an annual production capacity of 34.8 million tons (2016). EG is primarily used in the synthesis of polyester fibres and PET bottles (> 80%), while other uses include antifreeze [4].

Specific Objectives

The main objectives of this project is to build a mechanistic understanding of the sugar cracking process to reduce risk during scale-up. This includes

- Investigation of the effect of operating conditions
- Obtain a deeper understanding of the chemical reaction network and important physical aspects of the process
- Development of a kinetic model that can predict product yields

Experimental

A simple schematic of the laboratory setup for the sugar cracking process is shown in Figure 1. The bubbling fluid bed reactor is loaded with particles and is fluidized with nitrogen. The aqueous glucose solution is sprayed into the hot reactor operated at 525 °C and 1 atm using a spray atomizer. The feed is rapidly heated and the glucose molecules are cracked to produce smaller fragments. The product vapors are carried out of the reactor and are passed through a condenser, where the liquid product is condensed. The condensed liquid product is analyzed using HPLC to quantify the yield of oxygenates.

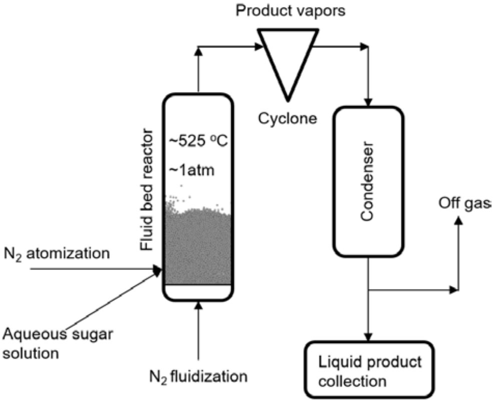

Figure 1: Simple schematic of laboratory setup for the sugar cracking process.

Kinetic model

It is of interest to build a kinetic model that can predict the product yields from the process. Seshadri & Westmoreland [5] calculated reaction kinetic parameters for a number of reactions related to glucose pyrolysis using gas-phase quantum-chemistry and statistical-mechanics calculations. Based on these calculations, a reaction network has been set up assuming instantaneous evaporation of the aqueous glucose droplet and heating to the reactor temperature. The model solution as a function of residence time is shown in Figure 2.

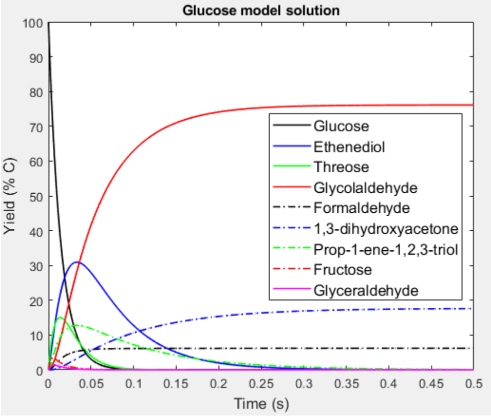

Figure 2: Example product distribution from kinetic modelling of glucose decomposition.

Experimental Results

An example of the product distribution from lab-scale sugar cracking of glucose is shown in Table 1. Here it can be seen that glycolaldehyde is produced in yields as high as 74 wt%, and the main by-products are pyruvaldehyde (9 wt%) and formaldehyde (7 wt%), along with minor byproducts such as acetol and glyoxal.

Table 1: Comparison of experimental and model yields in wt% carbon.

		Exp.	Model
C3	Pyruvaldehyde	9%	N/A
	Acetol	2%	N/A
	1,3-dihydroxyacetone	0%	17%
C2	Glycolaldehyde	74%	77%
	Glyoxal	2%	N/A
	Acetic acid	1%	N/A
C1	Formaldehyde	7%	6%
	Sum	95%	100%

Discussion

From table 1 it can be seen that the yields of glycolaldehyde and formaldehyde calculated by the model agrees well with the experimental data. However, the model is limited with respect to the C3-products. The model predicts 17 wt% yield of 1,3-dihydroxyacetone, whereas pyruvaldehyde and acetol are the experimentally observed C3-oxygenates.

However, it should be noted that the model includes only few secondary decomposition products, and further decomposition of glycolaldehyde and other oxygenate products are not included.

Conclusions

Sugar cracking of glucose is a promising process for production of chemicals from a renewable source. Glycolaldehyde can be produced with yields as high as 74 wt%. Glycolaldehyde can be hydrogenated in a second step to produce EG, which is a large commodity chemical.

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Waste Recycling in an Integrated Melting Furnace

(August 2015- February 2020)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Stone wool is produced using natural stone as a raw material. The material is melted and spun into fibers [1]. The fiberized product can be re-melted and fully recycled back into the stone wool production process.
The recycled stone wool waste comprises waste from the production, waste generated during installation of products and waste resulting from renovation and demolition of buildings. This project aims at investigating fundamental differences in melting behavior of stone raw materials and stone wool waste as well as the effect of introducing increased amounts of stone wool waste in the melting process of stone wool production.

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Abstract

This study focuses on the recycling of stone wool waste into the melting process of stone wool production. The fundamental differences between the natural stone raw materials and the recycled stone wool waste is investigated through lab studies of melting temperature and melting energy cost. Full-scale measurements of an Integrated Melting Furnace (IMF) in production is carried out to investigate the effect of increased recycling on the melting process.

Introduction

The Integrated Melting Furnace (IMF) is a new technology invented for the purpose of creating the 1500°C melt required in the stone wool production process. The IMF comprises two pre-heater cyclones and a melting cyclone. A sketch of the melting cyclone is seen on Figure 1. Inside the melting cyclone a tangential inlet of materials, air and fuel generates a swirling combustion inside the cyclone.

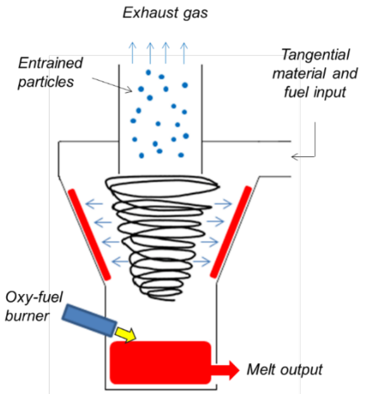

Figure 1: The melting cyclone of the IMF. Materials are blown in tangentially along with air and fuel, creating a swirling flow. Molten material collects in the melt bath in the bottom, superheated by oxy-fuel gas burners.

As the environment inside the melting cyclone is extremely harsh, and feasible methods for measuring inside the melting cyclone has not yet been found. Therefore, the melting process will be studied by particle sampling in the flue gas above the melting cyclone. The particle flux and properties of the entrained particles in the flue gas will be analyzed in order to indirectly add to the understanding of the processes taking place inside the melting cyclone.

Specific Objectives

The aim of the project is to understand the behavior of recycled stone wool waste in the IMF. This will be done through the following steps:

i) Material characterization of a conventional stone wool charge and recycled stone wool waste
ii) Particle sampling and full scale tests on an IMF production plant
iii) Building a mechanistic process model

Results and Discussion

A lab study on the melting behavior of the conventional stone feed and recycled materials was carried out using hot stage microscopy (HSM) and Differential Scanning Calorimetry [2]. The HSM study showed that the melting temperature of stone wool waste is at least 50°C lower than the stone feed, as can be seen from the resulting images in Figure 2. DSC showed that the energy consumption of melting stone wool waste is roughly 20% lower than that of the studied stone feed.

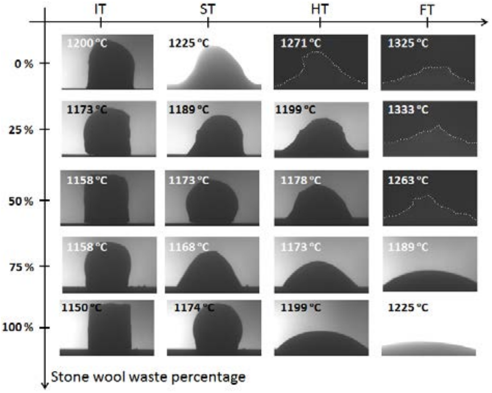

Figure 2: Samples comprising conventional stone wool charge and stone wool waste is analyzed using HSM [2]. The following characteristic shapes are identified during the measurements: Initial Deformation (IT), Spherical Temperature (SP), Hemispherical Temperature (HT) and Flow Temperature (FT). The heating rate was 5 K/min.

Particles have been sampled from the flue gas stream by use of an isokinetic suction probe, in which a part stream of the flue gas is sucked through a probe. Upon entrance to the probe, the gas is immediately cooled down, so that the particles will solidify, avoiding agglomeration of particles inside the probe. The particles are filtered out in a small cyclone. An example of the sampled particles is seen in the SEM image on Figure 3. Mainly two particle types are seen: dark gray porous particles and spherical particles in a lighter contrast. Energy-Dispersive X-ray spectroscopy (EDX) reveal that the porous particles consist of mainly carbon and is thus identified as unburned coal. The spherical particles have chemical compositions like that of the stone wool products. The spherical shape indicates that this is material that has been molten. It is however not possible to distinguish between molten droplets originating either from the stone-based feed or from stone wool waste. Thus, it is not possible to determine if the main origin of these entrained particles escaping the melting cyclone is the stone raw materials or the stone wool waste. It is however proven, that both material types have had a long enough residence time inside the melting cyclone for them to melt.

Future work

In order to determine whether stone raw materials or stone wool waste show different likeliness towards escaping the melting cyclone, a series of particle sampling experiments has been carried out a various IMF process settings where the stone wool waste dosing has been varied.
Statistical analysis of the obtained flux of entrained particle analysis will hopefully give clear answers.

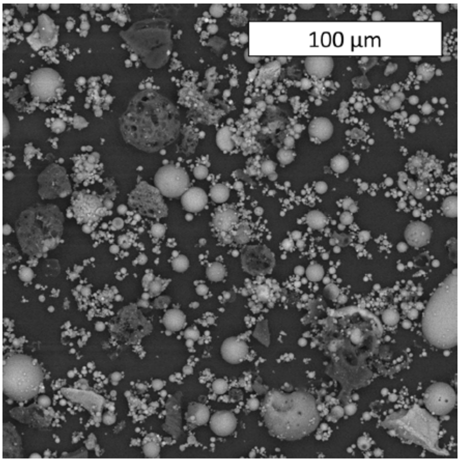

Figure 3: SEM image of sampled particles obtained via an isokinetic suctioning probe inserted into the flue gas above the melting cyclone of an IMF.

A mechanistic model is currently being constructed in order to analyze the material flow streams of the IMF. The model is based on the conventional cyclone model by Muschelknautz and co-workers [3,4]. Comparison between the measured flux of entrained particles and the model predictions will be carried out with the ultimate goal of understanding the difference in behavior of stone raw materials and stone wool waste inside the IMF.

Acknowledgements

This project is a collaboration between the CHEC research center at DTU Chemical Engineering and ROCKWOOL International A/S. The financial support from Innovation fund Denmark under Grant number 5189-00019B is gratefully acknowledged.

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List of Publications

1. V. Schultz-Falk, K. Agersted, P. A. Jensen, M. Solvang, Journal of Non-Crystalli4ne Solids, 485 (2018) 34-41

Renewable Synthesis of Higher Alcohols from Syngas over Rh based Catalysts

(January 2017- January 2020)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

A sustainable and free of fossile fuels future energy supply is anticipated to widely depend on renewable energy sources (e.g. wind, solar energy). Periodic fluctuations in the energy input rise the demand for efficient ways to store excess energy. Power-to-chemical concepts as one possible solution involve the direct conversion of harvested energy through water-electrolysis to produce H_2 which is then subsequently converted into chemical energy carriers with more favorable storage properties. Hereby, the catalytic reaction of carbon oxides and hydrogen to ethanol is of interest and is investigated in this PhD project.

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Abstract

Catalytic reaction testing of SiO_2-supported Rh catalysts with a wide span of crystal sizes revealed a clear structure dependence for the production of C_2-oxygenates (C_2-O) from CO and H_2. Hereby, small Rh crystals showed to be more favorable in the selective conversion of syngas to C_2-O whereas larger crystals dominantly produced hydrocarbon products. The observed increase in overall activity with increasing particle size, combined with simple statistical models on the distribution of different crystals facets, suggests that often assumed under-coordinated Rh sites may not constitute active sites for C-O bond cleavage.

Introduction

The direct conversion of syngas to C_2-O is limited to few catalytic single-metal systems, with supported Rh catalysts striking by a high ability to solely produce desirable C_2-O compounds and suppress the formation of unwanted by-products. A widely assumed reaction mechanism for the formation of acetaldehyde and ethanol as the two major C_2-O derivatives comprises dissociative CO adsorption, creating alkyl species, as well as molecular adsorption of CO, coupling with CH_x to then form the molecular carbon-carbon-oxygen skeleton of the target molecule [1]. Breaking the carbon oxygen bond is considered as the reaction rate determining step. Hence, to increase the overall activity of this comparably slow reaction, a better understanding on the nature of the catalyst sites that are involved in activating CO may be beneficial for a more rational design of better catalysts.

In this direction conducted theoretical calculations indicate under-coordinated Rh sites to constitute the active centers for C-O bond scission, whereas CO activation on close-packed surfaces is kinetically highly unfavorable [2]. Low-index planes were suggested to be responsible for the selective coupling and hydrogenation of dissociated CO and intact CO molecules towards C_2-O products [3]. The implication from this concept is that very small Rh clusters (around 2-3 nm), characterized by a high fraction of under-coordinated sites, would exhibit a high activity and a comparably low selectivity in forming C_2-oxygenates. Vice versa, large crystals, being dominated by close-packed crystal planes, would be expected to reveal a low overall activity in CO hydrogenation [4].

The observed wide-spread of experimental results in the literature does not unambiguously support such a concept. Herein, results indicating a size-dependent behavior for Rh/SiO_2, with small Rh particles being more selective in forming C_2-O but less active than larger ones [5], observations indicating a structure-independent behavior [6] and single crystal studies revealing the requirement of step sites to activate CO [7] can be found. Thus, the there is a continuous need for further experiments to unravel the origin of an eventual structure-dependent behavior in CO hydrogenation over supported Rh nanoparticles.

Specific objectives

Key objective of this project is to gain further insights into the reaction mechanism underlying the formation of C_2-O products over Rh based catalysts. Hereby, focus is set on unravelling of anticipated key reaction steps (e.g. C-O bond scission, coupling of CO and CH_x) and their possible structure as well as support effects.

Experimental methods

In brief, Rh/SiO_2 catalysts were prepared by different methods to obtain a library of differently sized SiO_2-supported and unsupported Rh crystals. Employing wet impregnation of $Rh(NO_3)_3$ onto SiO_2 with nominal loadings of 0.5 to 20 wt% yielded Rh crystals with ca. 2-5 nm in diameter. To extend the range of investigated sizes, a colloidal synthesis approach was followed. Hereby, Rh/SiO_2 catalysts with ca. 5 and 8 nm sized Rh particles were obtained. Residual capping agents from the synthesis were attempted to be removed by rapid thermal annealing. Further, direct reduction of different Rh metal precursors ($RhCl_3$, $Rh(NO_3)_3$) yielded large crystals (ca. 100 nm according to Brunauer-Emmett-Teller (BET) surface area) which were then diluted with SiO_2 before reaction testing. Mean crystal sizes as plotted in Figure 1 were estimated based on transmission electron microscopy (TEM) imaging analysis and results from H_2-chemisorption double isotherm measurements.

Results and Discussion

Obtained results from catalytic reaction testing of catalyst samples with different Rh mean sizes underline a structure-dependent behavior for the catalytic formation of oxygenate products. The ratio of activity in forming C_1-/C_2-O compounds relative to the overall activity exhibits a clear, to the particle size inverse correlation (Figure 1). The observed transitions between different products with varying Rh diameter, C_1-O only being formed in the size range of up to ca. 2-3 nm, C_2-O being detected with significant selectivity values also for medium-sized Rh nanocrystals and a with particle size increasing selectivity in forming hydrocarbons, are in good agreement with the reported results from Arakawa et al. [5]. Further, a significant increase in the overall activity was observed with increasing particle size, pointing towards a structure dependence of the overall reaction rate determining reaction step. In this context, the activity of larger Rh crystals (d_p > 10 nm) would be of interest. Possible continuations may be a decrease of the total activity, outlining an optimum particle size for the CO activation, or a rather constant TOF value for larger crystals, indicating the transition into a structure-independent size range. The latter scenario is known from Fischer-Tropsch metals.

Table 1 summarizes TOF values that were obtained for large, unsupported Rh crystals. Hereby, a strong difference in activity was observed depending on the choice over the Rh precursor. Similar BET surface areas and the absence of structural differences as inspected by TEM imaging does not provide an explanation for the observed difference in activity. Based on the obtained TOF values, no clear conclusion on the true intrinsic activity of large Rh crystals may be possible and will require further experiments, inspecting the potential role of possibly residual chlorine and thereby caused changes to the catalytic properties.

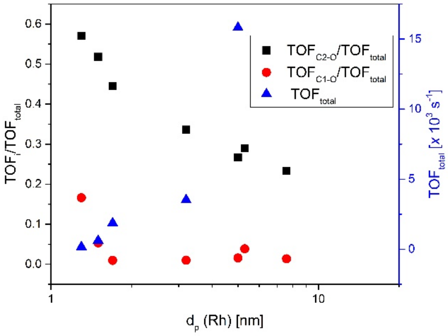

Figure 52: Turn-over frequency (TOF) values for the formation of oxygenates relative to the total activity as obtained from differently sized SiO_2-supported catalyst under CO-H_2 reaction testing (250 °C, 20 bar CO/H_2 (V/V, 1/2)).

Table 7: TOF values for unsupported, SiO_2-diluted Rh crystals from different precursors during catalytic CO-H_2 reaction (250 °C, 20 bar).

Rh precursor	TOF_{total} [s^{-1}]	TOF_{C2-O} [s^{-1}]
$Rh(NO_3)_3$	$2.2 * 10^{-4}$	0
$RhCl_3$	$4.3 * 10^{-2}$	$1.0 * 10^{-4}$

Conclusions

CO hydrogenation to C_2-O products reveals to be highly structure dependent for Rh/SiO_2 catalysts, showing a preferential formation of oxygenates over small Rh clusters whereas hydrocarbons constitute the main products over larger Rh particles. Opposite hereto, the activity in dissociative CO activation follows the particle size. Thus, the in this work obtained experimental results do not directly support a possible assignment of C-O bond scission to under-coordinated Rh sites. It is rather suggested that the CO insertion step may possibly rely on high index crystal planes, causing the observed particle size effect.

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Anticorrosive Barrier Coatings

(September 2017- August 2020)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Contribution to the UN Sustainable Development Goals

Developing new coating formulation for coating industry can lead to coatings that are more functional. Anticorrosive coating lifespan can be increased by tuning coating ingredients such as pigments and binders. The innovative use of pigments and adjusting pigment parameters in barrier anticorrosive coatings can increase the efficiency of anticorrosive properties, thereby prolonging the lifetime of protected structures and increasing the time between reconstructing.

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Abstract

Corrosion is one of the most noticeable reasons for catastrophic failures in buildings and equipment; and threaten structures safety. The application of coatings is a very economical method for controlling and delaying corrosion in metals. Approximately 90 percent of all metal surfaces are covered by organic coatings. The combination of organic coatings and functional pigments can improve the protection ability of coatings. The aim of this work is to develop the performance of an anticorrosive primer by controlling pigment parameters like shape and size distribution at different reduced pigment volume concentrations.

Introduction

Beside the cost of corrosion, the structural failure of the different industrial structures make the protections against corrosion very vital especially in the presence of chloride. An anticorrosive coatings system usually consists of multiple layers with different properties and purposes. Depending on the required properties of the coatings system, the individual coat can be metallic, inorganic or organic. The common system build-up consists of a primer, a mid-coat and a top coat. For better protection against corrosion, some functional pigments are added. The function of the primer is to ensure good adhesion to the substrate and to protect the substrate from corrosion. [1]. The anticorrosive pigments can be divided into three main categories including inhibitive, barrier and sacrificial pigments [2]. All studies have indicated that coating properties depend on pigment characteristics, such as chemical nature, particle size, state of dispersion, morphology and the reduced pigment volume concentration (Λ) which is the ratio of pigment volume concentration (PVC) to the critical PVC [3], [4], [5].

$$\Lambda=PVC/CPVC$$

Barrier pigment

The aim of barrier coatings is ideally protection of the substrate metal, by providing an impervious barrier to corrosive species and moisture. Two possible mechanisms can be responsible for the barrier property of a coating. One is blocking the path for cations to reach the substrate and the other one is preventing external flow between cathodic and anodic sites by means of a high electrical resistance coating [6].

Pigment engineering

"Pigment engineering" can be defined as controlling and triggering pigment properties in a systematic way. The most effective pigment parameters on the functionality of the coatings are illustrated in Figure 1.

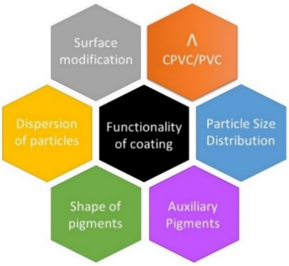

Figure 53: Effective parameters in pigmentation

The reduced PVC is one of the important parameters in triggering the coating properties. Below and above CPVC, the coating properties such as permeability change drastically. For designing a good barrier coatings, the PVC usually is adjusted below CPVC. The shape and size of pigments closely affect the barrier properties. The outstanding barrier properties of lamellar pigments were reported in different studies. Probably the best-known example of the use of lamellar pigment (Micaceous Iron oxide – MIO), is the protection of Eiffel tower in Paris. The size of pigment and more important the particle size distribution has an important effect in packing factor of the pigment and as a result on the barrier properties of the coatings. Particle dispersion is very important as well for having a good barrier property in all area of coating film. Parameter of the hexagons in Figure 1 are coupled to each other.

Specific objectives

The main objectives of this project are to increase the functionality of AC coatings by triggering the pigment parameters. The focus of this work will be on the coatings, which contain barrier pigments. During this study, these two hypotheses will be followed:

1) Maintaining Λ below critical value (perhaps 0.7), while increasing packing factor will lead to better barrier properties of anticorrosive coatings.

2) Increasing aspect ratio and/or surface area of lamellar pigments, improve the barrier properties of anticorrosive coatings.

Experimental

During this study the pigment parameters such as oil absorption, particle size distribution and surface are of pigments were measured according to ASTM-D281 and ASTM-C1070 [7], [8].

During this study, the focus was on the barrier property of the coatings. The barrier property of coatings during this study is examined trough delamination test and diffusion cell.

For the coating delamination measurement a 50 mm vertical scribe with a width of 2 mm was centered on the front of each panel. The specimens were exposed to 3.5 wt% sodium chloride solution at an angle of 75 to 80°. For measuring the delaminated region, a sharp knife was used to remove the delaminated coating from the surface.

The diffusion cell dimensions which was used, are 150×80×80 mm^3 (Figure 2). The liquid volume in the receiver and donor chambers are 33.1 cm^3 and 92.1 cm^3. The effective coating area for diffusion is 9.1 cm^2. A Metrohm 781 pH/Ion meter was used in this research for tracking the ions trough the diffusion cell. For measuring the ions, a sodium-selective glass membrane electrode and a reference electrode (LL ISE) were used.

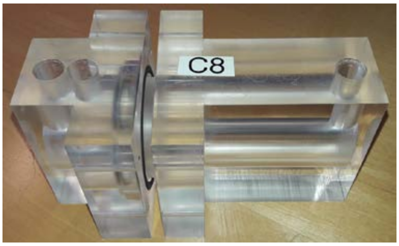

Figure 54: The used diffusion cell in this study

Conclusions

Pigment engineering is a noticeable potential for improving anticorrosive properties of coatings. By triggering pigments parameters it is possible to improve the coatings properties by using same pigments as before. During this work, it will be tried to figure out the effect of pigment parameters on the corrosion resistance of epoxy coatings, which contain barrier pigments.

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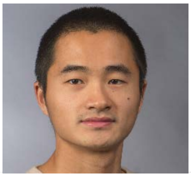
Stretchable conductive elastomers

(January 2018- December 2020)

Contribution to the UN Sustainable Development Goals

In this project, a new method is proposed to fabricate stretchable conductive elastomers. The approach is simple, fast, scalable, and cost-effective and can be easily applied to other materials. With this method, a conductive elastomer, with high conductivity can be produced with less conductive material by processes that are easily up-scalable compared to currently used technologies. Therefore this project contribute to UN Sustainable Development Goal no. 12 ---Responsible consumption and Production.



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Abstract

As the potential for next generation electronic devices, stretchable conductive materials have been widely studied. One critical challenge lies in maintaining conductivity while achieving high stretchability. In this study, a simple and effective method has been developed to produce stretchable conductive material. Results show that the conductivity of prepared materials can be maintained even when tensile strain reaches 160%, which means that the prepared material is a good candidate for flexible electronics.

Introduction

Recently, stretchable conductive materials (SCM) have gained extensive attention from researchers because of their potential applications in wearable electronics and biomedical devices [1,2]. One of the key challenges in realizing those applications is that SCM have ability to maintain stable conductivity under large level of strain [3].

As a popular matrix for SCM, polydimethylsiloxane (PDMS) has gained considerable attention due to the unique properties, such as biocompatibility and superior elasticity [4,5]. However, the application of PDMS is restricted by its poor electrical conductivity. To improve the conductivity of PDMS, one popular way is burying conductive networks into the PDMS matrix by directly dispensing conductive particles, such as carbon nanotubes (CNTs), in matrix with sonication [6]. On the one hand, network- based SCM are feasible for large-scale production. On the other hand, network- based SCM suffer from poor stretchability, especially for high aspect ratio particles based SCM [7]. Another critical challenge for network- based SCM is that electrical conductivity drops rapidly with increase of tensile strain [8].

In this study, a simple and effective strategy to fabricate SCM is presented, which integrates multi-walled carbon nanotubes (MWCNTs) and PDMS. Experiment results show that the prepared SCM not only provide comparable conductivity as reference samples but also have better stretchability than reference samples. Moreover, the normalized resistances (R/R_0, where R is resistance at certain strain and R_0 is the resistance at zero stress state) of prepared SCM show tendency of decreasing under tensile strain, which is completely different from the results of reference samples. Therefore, this novel SCM can be a desirable candidate for next generation electronics.

Specific Objectives

This project aims at developing new methods to prepare SCM, which can undergoing large deformations while the electrical performance is maintained.

Methodology

SCM based on bimodal networks have been prepared. Firstly, MWCNTs were entrapped in a hyper-branched short chain PDMS (SC-PDMS) to form high conductive domains. Secondly, hyper-branched long chain PDMS (LC-PDMS) has been introduced as the surrounding matrix. Additional MWCNTs were added into LC-PDMS as the “bridge” to connect the highly conductive domains. Thirdly, entrapped MWCNTs and hyper-branched LC-PDMS were mixed together and cured under high temperature to prepare the final composites. Reference samples were also prepared by roll mill and ultra-sonication (conventional system).

Results and Discussion

Figure 1 shows the comparison of stretchability and conductivity of samples prepared by different methods. As it can be seen, a SCM based on bimodal networks (BS sample) has a conductivity comparable to as a well dispersed sample with uniformly dispensed MWCNTs (conventional system, CS sample), while both samples show much better conductivity than a corresponding roll milled sample (RM sample) (10 times better). As for the elongation at break, the BS sample shows obvious advantages over reference samples with a significantly higher elongation at break.

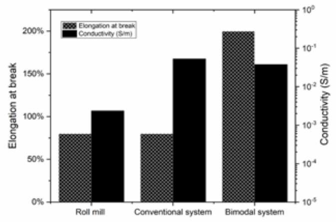

Figure 1: Comparison of stretchability and conductivity of samples prepared by different methods.

On the one hand, because of the localization of most of the MWCNTs in the SC domains, the stiffness of BS sample did not increase significantly, despite addition of MWCNTs, which leads to the improved elongation at break compared to the reference samples. On the other hand, highly conductive domains were formed by entrapping MWCNTs in the SC-PDMS. When small amounts of MWCNTs were additionally dispensed in the LC-PDMS, those MWCNTs acted as conductive wires and connected the high conductive domains to form conductive networks.

Figure 2 shows the changes of normalized resistance of samples prepared under different conditions. It can be observed that the BS sample shows a different tendency of normalized resistances under strain while all the reference samples have increased normalized resistances with increase of strain (as would be expected).

This could be explained by the unique bimodal network structure in the BS. For all of the other systems, including systems prepared using heptane (CS- heptane sample) and toluene (CS- toluene sample) as dispersing solvents, when force was applied on the samples, the conductive networks formed by uniformly dispensed MWCNTs were gradually destroyed due to the deformation of the samples. Therefore, the normalized resistances of RM sample and CS samples increased with increasing tensile strain. For the BS, we hypothesize that the uniformly dispersed MWCNTs in the LC-PDMS acted to connect the highly conductive domains, resulting in a maintained conductivity at high strains. In addition to this, it can be observed that the normalized resistances of BS sample decreased instead of increased with increasing tensile strain, illustrating a significantly different conductive network in the BS.

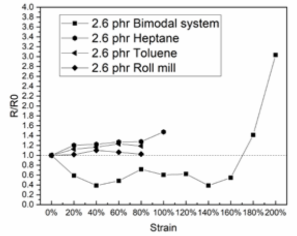

Figure 2: Changes in normalized resistance of prepared SCM composites and reference samples under different strains.

However, when the strains exceeded 160%, even the percolated pathways in the BS were also destroyed, leading to an increase in the normalized resistances of also these samples until reaching its strain limitation.

Conclusions

The current work has shown that it is feasible to prepare SCM with high conductivity and high stretchability. With this method, the future work will be focused on the applications of this novel material.

Acknowledgements

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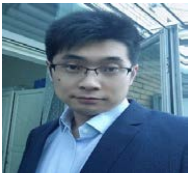
Preparation and Characterization of Hard-Soft Thiol-ene Materials with Strong Interfacial Properties

(December 2016- December 2019)

Contribution to the UN Sustainable Development Goals

Innovation advances the technological capabilities of industrial sectors and prompts the development of new skills. The layer-by-layer (LBL) technique has received significant scientific and technological interest as an effective and powerful approach to prepare materials with specific properties. A new step-by-step method to produce homogeneous material with different mechanical properties was developed and investigated. The research is very promising for the development of materials having multiple mechanical properties.



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Abstract

Thiol-ene materials are a series of materials that can easily be crosslinked using a suitable photo-initiator and a UV light source. An advantage of thiol-ene materials is that they can be tailored to have specific mechanical properties by controlling the stoichiometry of the mixtures. Tetrakis (3-mercaptopropionate) (**PETMP**) with 1, 3, 5-triallyl-1, 3, 5-triazine-2, 4, 6(1H, 3H, 5 H)-trione (**TATATO**) as the hard segment exhibited strong tensile and compressive strength but had low elongation and weak bending stiffness. A mixture of PETMP and trimethylolpropane diallyl ether (**TMPDE**) was selected as the soft segment. The alternating hard and soft thiol-ene material with a strong interface was successfully prepared and characterized by filament stretching rheometry (**FSR**) and atomic force microscopy (**AFM**).

Introduction

Thiol–ene materials can be obtained through traditional thermal conditions with common azo-species such as 2,2-azobis(isobutyronitrile) (**AIBN**) or via with little or no added photo-initiators photochemical thiol–ene reaction methods.[1] Thiol-ene materials are formed through highly efficient reactions of thiols with reactive C=C bonds; they have broad application in hydrogel drug delivery, coatings, adhesives, optical applications, dendrimer synthesis, all-solid-state electrolyte, high strength laminates, dental resins and electroluminescent films. Two thiol reactions emerged, thiol–ene free-radical addition to electron-rich/electron-poor C=C bonds, and the catalyzed thiol Michael addition to electron-deficient C=C bonds. Unlike typical chain-growth free-radical polymerizations or step-growth condensation polymerizations, thiol-ene polymers form in a stepwise manner but their formation is facilitated by a rapid, highly efficient free-radical chain-transfer reaction.

The interface between the two polymers in LBL systems plays an essential role for the overall mechanical performance of such systems. In particular, the mechanical properties of the interface are crucial to the usability. Insufficient interfacial adhesion between the two polymers leads to fracture during elongation or impact; such materials often exhibit initial fracture at the interface or near the interface[2]. Typically, such interfaces can be reinforced by use of copolymers to increase the bond strength between the two polymer phases. The poor mechanical properties were caused by an unstable phase morphology and poor interfacial adhesion. Another procedure applied is to reinforce interfaces by increasing the temperature above the glass transition temperature or melting point after the LBL materials were prepared, so that the interface of the two materials fuses together. We used a step-by-step method to produce a homogeneous material with different mechanical properties.

Preparation of rods with hard-soft interface

We prepared column shaped samples having a sandwich structure with alternating hard and soft segment polymers. The hard segment polymer liquid was prepared by using the ratio (1:1) of PETMP to TATATO.

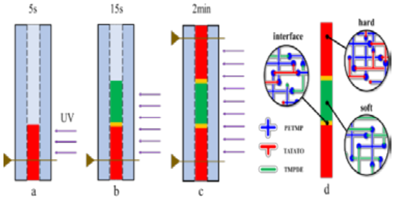

Figure 1. The production process (**a-c**) for a 10mm soft segment hard-soft alternate sample, **d.** The structure of soft-hard alternate material

The soft liquid was obtained in the same way except for replacing the TATATO with TMPDE. A syringe needle was impaled into the bottom of the mold through the diameter (**Figure 1a**), and then the hard segment polymer liquid was slowly poured into the mold by using a 10ml syringe. The mold was placed in a vacuum drying oven to remove air bubbles at room temperature, when the liquid level raised to 10cm (base of the needle). After that, the mold was exposed by ultraviolet light (10mW/cm^2, λ =365nm) for 5seconds. After two injections and illumination, a cylindrical hard-soft alternate sample could be obtained after removing the needles and demolding.

Results and Discuss

The rheological measurements were carried out using a filament stretching rheometer (VADER 1000 from Rheo Filament ApS) with a strain rate of 0.001s^{-1}[3] (**Figure 2a**). All experiments were performed at room temperature. The high-speed camera was used for recording the images of the fracture process., the crack was generated in the soft segment surface; not in the interface of the hard and soft material (**Figure 2b,2c,2d,and 2e**).

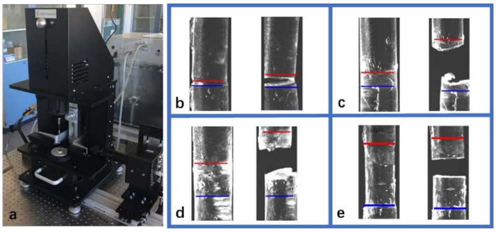

Figure 2. a. The filament stretching rheometer VADER 1000 from Rheo Filament ApS; The image of **b.**1mm, **c.**2.5mm, **d.**5mm, and **e.**10mm soft segment alternate materials fracture process (blue line shows the bottom interface, red the top)

The surface properties of the hard and soft segments as well as the interface were evaluated by AFM (Nano Wizard 3, Germany).[4] The sensitivity of the cantilever was calculated based on a measurement against a bare silicon wafer surface, while the accurate spring constant was obtained using a thermal noise method. The AFM cantilever scan the material surface from hard(left) to soft(right) across the interface with a conic tip in half angle 20 ° under 1.5 ± 0.5 MPa. As shown in the height images of **Figure 3b**, the hard segment surface has a similar height to the soft segment surface, but the interface is about 2μm higher than the plane of hard segment and soft segment because of swelling effect. The variation of the modulus is shown in **Figure 3c**; the hard segment (orange) has significant contrast to the soft segment (black). The interface shows red with an intermediate modulus, which varies continuously versus the distance of the hard and soft segment. The **Figure 3d** has the similar shape with **Figure 3c**, indicates the change of adhesion.

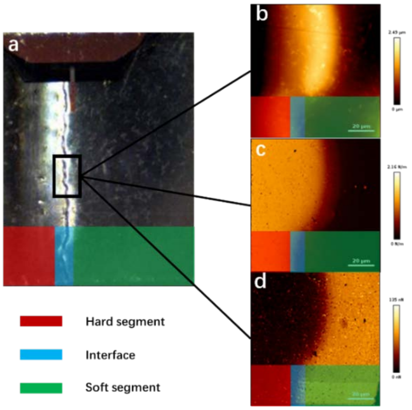

Figure 3. The junction surface of hard-soft material, (**a.** AFM images **b**. height channel, **c**. slope (measure of modulus), **d.** adhesion.) Obtained by Quantitative Imaging (QI) mode from the interface.

Conclusions

In summary, a new step-by-step pre-crosslinking method was designed to prepare hard-soft alternating thiol-ene materials. The overall mechanical properties of these materials are controlled by the interface between hard and soft segments. Compared to traditional LBL materials, the method significantly improved mechanical properties of the interface; hence, it can expand the application range of LBL materials considerably. The results provide a better understanding of how to improve the mechanical properties and a novel insight into rational design of controllable LBL materials. The alternate thiol-ene materials will provide a new promising strategy to develop multifunctional material. The materials can also be utilized in other fields, such as artificial joints and flexible robots.

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Depressurization induced gas production with CO_2-enriched air in multilayer hydrate sediment

(January 2018- December 2020)

13 CLIMATE ACTION

Contribution to the UN Sustainable Development Goals

The total global energy demand is on the rise rapidly. Ensuring everyone has enough access to energy is of great importance for the development of society. At the same time, the current energy system is facing challenges historically that carbon dioxide (CO_2) and other greenhouse gases are changing the global climate. Natural gas is regarded cleaner and more efficient than other fossil fuels, Accordingly, the generation of natural gas also helps cut reliance on the use of fossil fuels, thus significantly curbs the greenhouse effect.

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Abstract

Efficiently and safely producing natural gas stored as gas hydrates is an urgent and as yet unsolved challenge. CO_2 replacement method has the potential benefit of combining methane production and carbon dioxide storage. Injection of CO_2-enriched air is viable and economical compared with transportation of flue gas. In this study, a series of experiments were conducted where air and CO_2-enriched air were injected into simulated multilayer hydrate sediment. The experiments were conducted using a method that combines depressurization and CO_2-enriched air injection for methane recovery. Recovery rates are shown to increase when a three-stage depressurization method was introduced in the process at three different initial injection pressures at the same gas hydrate reservoir temperature. Compared with injecting air, injecting CO_2-enriched air promotes gas hydrate production. A multi-layer hydrate cap mechanism is proposed to describe the methane hydrate production combined with CO_2 storage.

Introduction

Natural gas hydrates are crystalline solids composed of water and gas molecules. Guests with different sizes, from small gases such as argon, nitrogen to quite large (butanes, methyl pentanes) are trapped into cages composed of hydrogen-bonded water molecules [1,2] It has been reported that significant quantities of natural gas hydrate exist in continental margin zones and permafrost areas[3,4]. How to efficiently and safely produce this tremendous amount of natural gas stored as gas hydrate remains an unsolved and urgent challenge.

A number of exploitation methods have been proposed based on the thermodynamic and physical characteristics of natural gas hydrate. Among the several production methods, depressurization is advantageous and has been studied extensively due to its energy-efficiency [5–8]. Furthermore, many field trials demonstrate the success of the depressurization method in producing gas from hydrate reservoirs. Another method which has been discussed for gas exploitation from gas hydrate reservoirs is a carbon dioxide (CO_2) replacement method via injection of CO_2 or mixtures containing CO_2. This technique has the advantage of both methane production and carbon dioxide storage in the marine sediment as gas hydrates that the idea here is that the chemical potential of methane hydrate is higher than that of CO_2 hydrate meaning that CO_2 hydrates are more stable. As a result, the injection of CO_2 into a hydrate reservoir can not only replace methane by CO_2 but should also reduce the impact of hydrate dissociation on geomechanically stability of the hydrate reservoir. In addition to the conventional one stage depressurization techniques, some depressurizations were experimentally performed in exceptional manners by investigators, for instance, slow stepwise depressurization, multistage depressurization and combination with thermal stimulation, water injection or gas injection.

In this study, we examined the factors which influence hydrate production from multilayer sediments by injection of air and CO_2 enriched air.

Recovery of CH_4 with simultaneous CO_2 storage was investigated. A combined production method was introduced where gas injection and depressurization are combined. Based on our experimental results, a hydrate mixture cap attenuation mechanism was proposed for gas production via depressurization with CO_2-enriched air for the first time. The results are of interest for development of a comprehensive description of gas hydrate production technology.

Results and discussion

In this research, two series of experiments were conducted by injection of air and CO_2-enriched air, respectively. Each of the series is under identical temperature to investigate the changes of reservoir pressure, gas production rates, and gas recovery ratios during methane hydrate production. Air injection experiments were conducted in multilayer sediment at injection pressures of 8.5 MPa, 10.2 MPa, 18.7 MPa, production temperature at 274.7 K. The recovery ratio of methane reveals the absolute recovery ability, which is in the light of the composition of increment of methane in the vapor phase. CO_2 in the vapor phase was captured simultaneously. Over the course of the production both methane recovery and CO_2 storage were gradually reach to a constant. It indicates that decreasing production pressure can significantly increase the recovery ratio of methane from the hydrate reservoir.

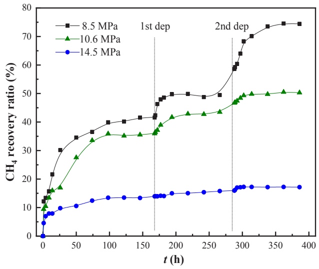

Figure 2:. Variation of the recovery of methane with time during the replacement process at different initial pressures and at 275.3 K.

CH_4 recovery and CO_2 storage at each end of stage are summarized in Figure 10. It is show that initial injection pressure has an influence on overall ratio even inconsistent of that on every stage.

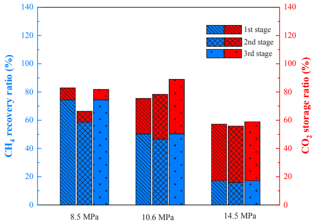

Figure *3*: Influence of injection pressure on CH_4 recovery and CO_2 storage ratio of different stages.

Conclusions

Results from experiments show that injecting air into methane hydrate reservoir is a feasible and potentially economical method for methane production but with low recovery. Injecting CO_2-enriched air demonstrated significantly increased production efficiency of methane while also storing CO_2. The introduction of step-wise depressurization can increase methane recovery.

Depressurization with gas injection significantly increased methane production efficiency, while its improvement on CO_2 storage performance is not clear. Based on the hydrate production behavior, a hydrate mixture cap attenuation mechanism was proposed for gas production behavior via depressurization with CO_2-enriched air for the first time.

Acknowledgements

This work is supported by the Department of Chemical and Biochemical Engineering, Technical University of Denmark and the State Scholarship Fund of China Scholarship Council.

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Enzyme immobilization for applications in membrane bioreactors

(June 2017- May 2020)

Contribution to the UN Sustainable Development Goals

The membrane bioreactor (MBR) is a highly relevant option in the development of sustainable production methods. Many fuels and fine chemicals may be produced in MBRs using enzymes as catalysts. The operation is energy efficient in that enzyme catalysis is typically operated at ambient conditions and with a low amount of by-products produced. The process intensification brought about by combining reaction and separation in one unit further adds to the energy efficiency of the process.

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Abstract
Enzyme immobilization on a solid support is applied to promote the stability and reusability of enzymes, thereby facilitating their use in industrial processes. Enzyme immobilization may be achieved by various methods and on different supports, the selection of which depends on the enzyme and process conditions at hand, as well as on the balance between enzyme stability and activity retention upon immobilization. The objective of this project is to design enzyme immobilization systems on inorganic membranes for use in membrane bioreactors. Inorganic membranes with ultra-high surface area and high thermal stability were produced from materials that showed high compatibility with the enzymes in question. Different immobilization methods are proposed and compared with respect to the catalytic performance of the enzymes upon immobilization.

Introduction

The ever-growing demand for sustainable processes and production methods is a motivation to continue developing new and improving existing enzyme immobilization systems for applications in membrane bioreactors (MBRs). The MBR offers a cost-effective and energy efficient means for the enzyme-catalyzed production of a variety of chemicals, including fuels and fine chemicals [1,2]. Enzymatic conversion is typically operated at a relatively low temperature and pressure, without the use of toxic chemicals and with a low amount of by-products produced, which results in an energy efficient process and simplified down-stream processing. The operation is further made cost-effective by reusing the enzymes in multiple reaction cycles as the enzyme can be retained within the reactor by the membrane while the products can freely pass through the membrane and to the permeate [3]. Nevertheless, one of the main complications involved in industrial applications of enzyme catalysis is the inevitable decay in enzyme activity. Enzyme immobilization has been proposed as a solution aimed at increasing enzyme stability as well as reusability [4]. For applications in MBRs, the enzymes may be immobilized on supports that are suspended in the reaction medium or they may be immobilized directly on the membrane [1,5].

In this project, we have explored the current state-of-the-art of enzyme immobilization for membrane bioreactor applications and we have identified gaps in which solutions to future green processes might be found.

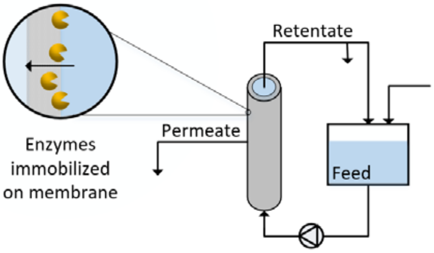

Figure 1. Membrane bioreactor with enzymes immobilized on membrane

Specific Objectives

Based on our investigation of current enzyme immobilization systems, our research comprises two main parts, covering two different aspects of enzyme immobilization on membranes: 1) Designing inorganic membranes with ultra-high surface area and tailor-made surface properties as support materials for enzyme immobilization. 2) Designing methods for enzyme immobilization on membranes that promote the catalytic properties of the enzyme and simultaneously allow high enzyme recyclability as well as reusability of the support materials.

Results and Discussion

To identify a suitable inorganic support material for enzyme immobilization, we studied the interactions between the enzyme alcohol dehydrogenase (ADH) and different inorganic support materials. Out of four different raw materials studied, powders of alumina and silica showed high compatibility with the enzymes, including high activity retention [6]. Subsequently, aluminosilicate nanofiber membranes were fabricated as support material for enzyme immobilization. The membranes offer a high surface area, which allows high enzyme loading and reaction efficiency. Furthermore, the high thermal stability of the inorganic membranes may be exploited to regenerate the native membrane properties by subjecting the membranes to thermal cleaning treatments. In the second part of the project, we propose and compare different methods for enzyme immobilization on membranes, namely, the common immobilization methods of physical adsorption and covalent bonding, as well as immobilization by polyelectrolyte layer-by-layer assembly and interfacial polymerization. The different enzyme immobilization methods are evaluated by a number of parameters, including enzyme stability and activity retention upon immobilization, recyclability and reversibility of the methods in order to regenerate the membrane support.

Conclusion

Enzyme immobilization on membranes for applications in membrane bioreactors is an attractive option in the design of sustainable industrial processes. The main goal of immobilization is to stabilize the enzyme and ensure its efficient use in multiple reaction cycles. The success of immobilization depends on the support materials used, as well as the immobilization method applied. Both these factors must be carefully selected for the system at hand with the aim of maximizing the lifetime of the enzyme while retaining high enzyme activity.

Acknowledgements

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List of Publications

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New Coating Systems for Durable and Highly Resistant Coatings

(December 2018 - November 2021)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Contribution to the UN Sustainable Development Goals

Corrosion is one of the biggest industrial challenges, which is not only a challenge from a financial and resource consumption aspect, but also a safety perspective.
Being innovative in creating new binders for coatings through hybridization will unlock new coating formulations for better protection of vehicles and structures. This would not only reduce the consumption of finite resources, but also improve human safety in industrialized areas.

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Abstract
Inorganic cross linked networks containing silicon has large potential in modern industrial coating systems. Their great affinity for metal and some polymers along with providing heat and abrasive resistance makes them very attractive for high durability systems. However, the curing mechanism of inorganic systems usually creates coating, which are too thin due to high-tension build-ups. The purpose here is therefore to make hybrid coatings where the attractive properties of silicon is merged into classic coating systems.

Introduction
Protecting metallic surfaces from degradation in our everyday life and in the industry is big business, accounting for roughly 3 - 3.5% of the gross domestic product in the United States.[1] Polymer based coatings films are used everywhere in the industry in as diverse applications as cars, floors or oilrigs. Purposes of applying coatings similarly vary broadly from e.g. anti-corrosion, anti-freeze or abrasion, heat and chemical resistance. Even with the many great properties the coatings imbue to surfaces, there is still room for improvement in both chemical capabilities and the actual coating application.
Industrial coatings are traditionally systems based on epoxies, polyurethanes and silicones working as a barrier between the substrate and the elements, on top of a primer, which provides the anti-corrosive component. These are usually build up in systems of layered coatings, which is ineffective procedure time and application wise.
A way to improve this would be to introduce inorganic elements such as silicon to the organic coatings. Inorganic coatings are known for their high substrate affinity, good abrasive and temperature resistance.[2] while not having the ability to create thick enough layer to be used effectively as barriers in industrial coatings. Via hybridization of the inorganic and the known systems, one could be able to achieve the best possible properties of the systems while dealing with the need for multiple coatings.

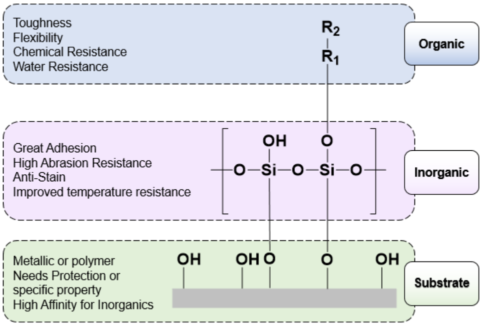

Figure 55: Schematic representation of an inorganic/organic silicon based hybrid coating system.

Specific objectives

The target of the project is to create hybrid coating systems combining known curing systems such as e.g. epoxy and silicone based systems.

- Establishing a core methodology
- Expanding the known systems
- Increasing the extend of hybridization

Establishing a core methodology

Firstly, basic knowledge must be compiled with respect to chemical modification of the inorganic binders within the frame of the project by investigating properties such as in chemical and thermal resistance, but with a particular focus on interfacial properties i.e. adhesion between substrate, coating and sequential layers of coatings.

Expanding the known systems

The project targets to expand these known systems by making hybrids, where better understanding of the interfacial phenomena will be exploited for formulation of new coating systems with superior performance. After establishment of curing methodology and initial properties, formulated systems will be prepared. The possibilities to apply prepared polymers as binders in coating formulations will be evaluated through testing and evaluation of the final coating systems, focusing particularly on surface properties as well as thermal and chemical resistance.

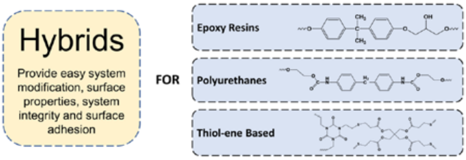

Figure 2: Hybrid binders as project deliverables for well-known coating systems.

Increasing the extend of hybridization

The project will initially aim to create optimized binder systems with excellent adhesion to substrate and organic coatings. From there the focus will switch to hybridization, creating hybrid primers with adequate coating properties and thickness. Thereby eliminating the need for successive coating layers. With the ultimate goal of creating a hybrid one-pot system, which covers the needs of a classic layered coating system.

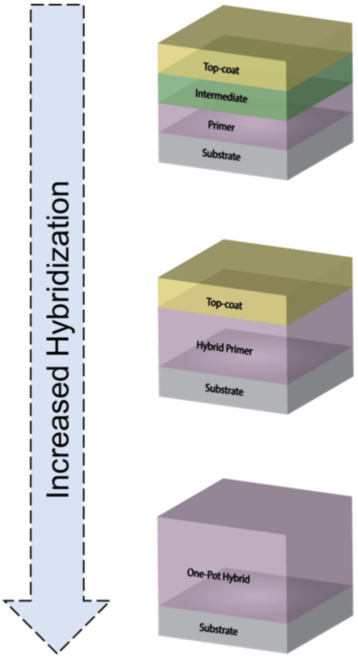

Figure 3: The elimination of the use of multiple layered coating systems through increased hybridization of classic and inorganic systems.

Acknowledgments

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High performance production of oligosaccharides by using enzymatic membrane reactors

(December 2018- December 2021)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Enzyme membrane reactor (EMR) is a novel technology for high quality oligosaccharides production. By applying enzyme catalysis and membrane separation, EMR reduces consumption of hazardous chemicals, organic solvents and energy in comparison with the traditional process of oligosaccharides fabrication. More importantly, product quality is better controlled in a simultaneous process of bioreaction and products purification, and prevents unexpected side reactions.

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Abstract

The PhD project aims at oligosaccharides production by using Enzyme Membrane Reactor (EMR) technology, with the final aim of narrowing the Mw distribution of products which greatly influence their properties and of course their value. Oligodextran, chitosan-oligosaccharides, fructo-oligosaccharides and heparin-oligosaccahrides with 10-15 monomer units are the initial target products in this project. Polysaccharides will be used as the substrates, which will be deconstructed by the relevant enzymes in the retention side while products with lower Mw will be collected in the permeate. Enzymes will be immobilized by different novel methods (polydopamine coating/electrospinning nanofiber) on/in the membrane in the EMR carrying continuously catalysis. Furthermore, in this study, interactions between enzyme/saccharides and membranes will be investigated to optimize the process.

Introduction

Oligosaccharides like oligodextran, chitosan-oligosaccharides, fructo-oligosaccharides, heparin-oligosaccharides show different properties (prebiotic activity, etc.) that depend on their molecular weight (Mw) [1-4]. Oligosaccharides with relatively low molecular weight (LMW) have been reported to exert important functions in immunology and are in some cases indicated for animal and human nutrition; therefore, these biomolecules have been widely used in medical, food and even cosmetic industry. Traditional production of oligosaccharides includes fermentation/extraction and chemical modification coupled with several steps of purification. Polysaccharides are normally obtained from plants via extraction, and in some cases such polysaccharides can be obtained from residues e.g. agricultural or urban residues. However, due to the occurrence of impurities in the biomass, fermentation is often conducted for obtaining specific polysaccharides, followed by chemical degradation. In the traditional process of degradation, glycosidic bonds are broken randomly by acid/alkaline agents, generating saccharides with shorter chains and also certain amounts of waste. Enzyme technology has alternatively replaced chemical degradation for oligosaccharides production due to their specificity on polysaccharides degradation under mild conditions, along with lower generation of wastes and undesired degradations. Combined with membrane technology, oligosaccharides can be generated and separated in-situ in an enzyme membrane reactor (EMR).

In previous works, high permeate flux with high shear stress on hydrophilic polyether sulfone (PES) membranes was found to improve the oligodextran Mw uniformity obtained, although a relatively low product concentration was collected in the permeates. Inspired by the fouling mechanism in the process, a 'fouling-induced' enzyme immobilization method successfully narrowed the membrane pores, enabling higher quality of the products [5]. Still, the low products yield due to membrane fouling and low enzyme loading efficiency are problems that need to be addressed.

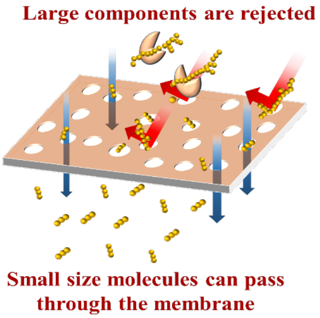

Figure 1. EMR for oligosaccharides production

Specific objects

The objects of this project are:

- Membrane modification to enhance anti-fouling ability and enzyme immobilization efficiency.
- Establishment of EMR that couples simultaneous enzyme reaction and separation for high quality oligosaccharides production.
- Understanding interaction between bioconversion and membrane separation for better control of oligosaccharides product quality.

Results and discussion

Membrane modification has been used to improve the filtration behaviour, particularly fouling. Polydopamine (PDA), due to its hydrophilicity, is able to decrease the fouling attachement of foulants during filtration.

Strong adhesion of PDA enable to create a coating layer on the membrane surface that facilitates enzyme immobilization. In this case, PDA helped improving membrane hydrophilicity together with enzyme loading efficiency, which resulted in higher productivity of the EMR.

Conclusion

Membrane modification that enhance both the membrane antifouling ability and enzyme loading efficiency enables a smart EMR design. With high bioconversion efficiency and selectivity, EMR shows great industrial potential in uniform oligosaccharides production.

Future work

Beside membrane modification, we will introduce electrospinning to establish a versatile platform for enzyme immobilization that enables smarter design of EMR, particularly in terms of immobilization possibilities. Tailored nanofibers exhibit many advances due to the specific properties (hydrophilicity, porosity etc.) of polymers [6]. Aiming at certain substrates and enzymes, electrospun fibers can be specially designed and modified for the purpose of enzyme attachment and encapsulation which will probably retain a high percentage of the enzyme activity along with high storage stability thus enabling an industrial application in the future [7]. In this project, electrospinning nanofibers will be used as immobilization matrixes in the EMRs. Additionally, the modified layer can also help to mitigate the effects of severe fouling [8].

Acknowledgements

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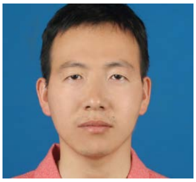
Modeling of Individual Activity Coefficients with the e-CPA EOS

(October 2016- September 2019)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

Due to the complexity and wide industrial application of the electrolyte solutions, both experimental and theoretical studies have attracted great interest. The investigation of individual ion activities is important for research of mineral and biological systems as well as for the validation of models for electrolyte solutions. This work presents a modeling study of individual ion activities in aqueous solutions of NaCl with the electrolyte Cubic-Plus-Association Equation of State. This work could provide supports for energy saving in industrial production of electrolyte systems.



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Abstract

The investigation of individual ion activities is important for research of mineral and biological systems as well as for the validation of models for electrolyte solutions. This work presents a modeling study of individual ion activities in aqueous solutions of NaCl with the electrolyte Cubic-Plus-Association Equation of State (e-CPA). With the adjustable parameters which are obtained by fitting the mean ionic activity coefficients, the e-CPA model can give good agreement for the mean ionic activity coefficients, but cannot provide accurate values for the individual ion activity coefficients.

Introduction

Over a long time, the investigation of individual ion activities has attracted considerable attention. This is because individual ion activity coefficients can be useful in the characterization of transport phenomena in electrolyte systems and are also helpful in our understanding of biological systems (sodium–potassium pump), membrane processes, as well as salting-in and salting out effects. The rest of this work is organized as follows: firstly, e-CPA EOS will be presented. Then the modeling results will be shown with all approaches, together with an analysis of the various contributions, discussion of the results and finally our conclusions.

Thermodynamic Model

Maribo-Mogensen et al. [1] extended the CPA EOS, which was proposed by Kontogeorgis et al. [2], to mixtures containing electrolytes. It includes the electrostatic contributions from the Debye–Hückel theory (which accounts for the long-range interaction of the ions), and the Born equation (which accounts for ion solvation).

In e-CPA, the ΔF is defined as the difference of 'Helmholtz energy divide *RT*' between aqueous electrolyte solution and reference state (pure solvent as the reference):

$$\Delta F = \left(\frac{A}{RT}\right)_{V,n} - \left(\frac{A}{RT}\right)_{V_0,n_0} \qquad (1)$$

And the expression for the contribution terms to activity coefficient of ion is given from the equation:

$$\begin{aligned}\ln\gamma_i = \left(\frac{\partial\Delta F^{SRK}}{\partial n_i}\right) + \left(\frac{\partial\Delta F^{Association}}{\partial n_i}\right) + \left(\frac{\partial\Delta F^{DH}}{\partial n_i}\right)_{\varepsilon_r} \\ + \left(\frac{\partial\Delta F^{Born}}{\partial n_i}\right)_{\varepsilon_r} + \left(\frac{\partial\Delta F^{DH}}{\partial\varepsilon_r}\right)\left(\frac{\partial\varepsilon_r}{\partial n_i}\right) \\ + \left(\frac{\partial\Delta F^{Born}}{\partial\varepsilon_r}\right)\left(\frac{\partial\varepsilon_r}{\partial n_i}\right) - \ln\frac{Z}{Z_0}\end{aligned} \qquad (2)$$

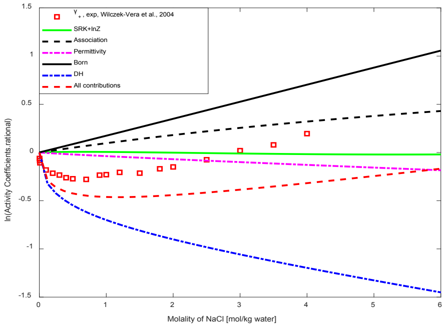
In Eq. (2), ε_r is the relative static permittivity of solvent in electrolyte solutions, n_i is the mole number of ion *i*, Z is the compressibility factor of solution, Z_0 is the compressibility factor of pure solvent.ΔF^{SRK} is the ΔF from SRK contribution, the ions have volume which cannot be ignored, and the volume-exclusion from ions is present, so, the SRK contribution is set for this. The term $-\ln\frac{Z}{Z_0}$ is a correlation of the compressibility factor, for the difference that based on mole numbers of ions and the one based on mole number of salts. Here, in our analysis we have combined $\left(\frac{\partial\Delta F^{SRK}}{\partial n_i}\right)$ and $-\ln\frac{Z}{Z_0}$ as 'SRK+lnZ' contribution. There is no association contribution for ions, but the association of solvent is affected by the presence of ions, so, the contribution from solvent association is also considered. $\Delta F^{Association}$ is the ΔF from the influence of solvent. We name $\left(\frac{\partial\Delta F^{Association}}{\partial n_i}\right)$as 'Association' contribution. ΔF^{DH} is the ΔF from ion-

ion interaction, we name $\left(\frac{\partial \Delta F^{DH}}{\partial n_i}\right)_{\varepsilon_r}$ as 'DH' contribution. ΔF^{Born} is the ΔF from ion solvation, we name $\left(\frac{\partial \Delta F^{Born}}{\partial n_i}\right)_{\varepsilon_r}$ as 'Born' contribution. It needs to be pointed that the relative static permittivity is composition dependence. When obtaining the chemical potential of ions by differential computing the residual Helmholtz energy, the differential of relative static permittivity should be taken account into. We combined $\left(\frac{\partial \Delta F^{DH}}{\partial \varepsilon_r}\right)\left(\frac{\partial \varepsilon_r}{\partial n_i}\right)$ and $\left(\frac{\partial \Delta F^{Born}}{\partial \varepsilon_r}\right)\left(\frac{\partial \varepsilon_r}{\partial n_i}\right)$ as 'Permittivity' contribution.

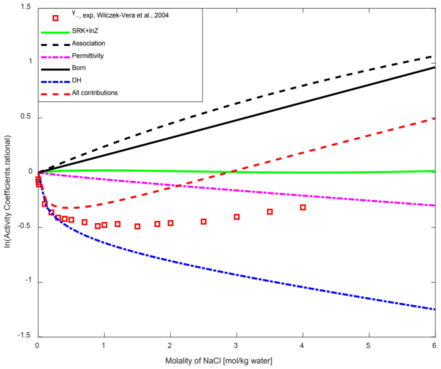
Modeling Results and Discussion

In this work, the individual ionic (and mean ionic) activity coefficients are calculated using e-CPA with the parameters from Maribo-Mogensen et al.'s work [1]. In e-CPA, the kinetic depolarization effect of dielectric constant is eliminated, and the Born radii are from Maribo-Mogensen et al.'s work [1], the ion radii from Marcus [3] are used.

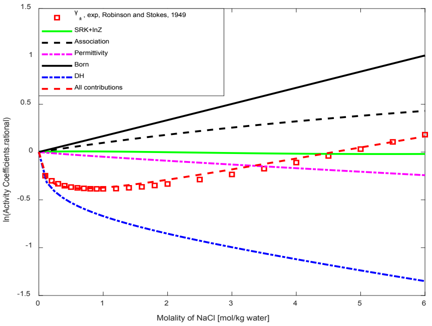
We present in Figure 1 both the complete results for e-CPA and an analysis of the individual terms for aqueous NaCl solution.



a. cation activity coefficients [4]



b. anion activity coefficients [4]



c. mean ionic activity coefficients [5]

Figure 1. e-CPA performance of activity coefficients for electrolyte solution of NaCl.

From Figures 1 (a) and (b), it can be seen that, the present version of e-CPA with the parameters optimized from mean ionic activity coefficients cannot provide accurate values for the individual ion activity coefficients.

What we observe is that there is an error for both cation activity coefficients and anion activity coefficient. The two effects cancel for the mean ionic activity coefficients. The DH and Born effects are still large and opposing. The 'SRK+lnZ' term is important, and affects the results significantly. Though the contributions from static permittivity are small, this contribution cannot be ignored. Finally, the association contribution is also of importance, especially at higher molalities (also the case for the SRK-term). The physical (SRK) and association terms have often (but not always) opposing trends (SRK negative and association positive), again especially pronounced at higher concentrations.

Conclusion

This work presents a modeling study of individual ion activities of NaCl in aqueous solutions by using the e-CPA EOS. The ion radius, Born radius, static permittivity and other parameters are critical in the calculations with e-CPA. More theoretical investigations are needed for the study of individual ion activities.

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Cyclone reactors: experimental and modeling study

(September 2016 - February 2020)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

Part of the research in this project investigates the use of Selective Non-Catalytic Reduction (SNCR), a relatively simple, cheap and well known solution, for cleaning the fluegas from combustion plants and how to make this more efficient. This can help developing countries reducing the adverse effect on human health from heat and power production without overburdening their economy with expensive high tech solutions that are only feasible in developed countries in the short term.

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Abstract

The main objective of this PhD project is to investigate important physical and chemical phenomena in cyclone reactors and to obtain an improved fundamental understanding needed for better utilization of cyclone reactors for industrial applications. This is achieved through experimental work in both pilot and industrial scale cyclone reactors, as well as through chemical reaction engineering modeling.

Introduction

Cyclone reactors are used in various industries for different applications, such as ore refining in the metals industry, raw meal preconditioning and emission reduction in the cement industry, and flue gas cleaning in the power industry.

A cyclone itself is a continuous and versatile separation device. The simple design makes it popular for application in harsh environments with extreme temperature, abrasion and corrosion.

Using cyclones as reactors provides an opportunity for process intensification. Furthermore, the highly turbulent swirling gas phase flow provides intense mixing as well as separation of the solid phase from the gas phase. Cyclone reactors can be used for both homogenous and heterogeneous reactions in and/or between the gas and solid phase.

The main principles of a cyclone reactor for a gas-solid system is sketched in Figure 1. Typically cyclone reactors have short gas residence times and longer particle residence times. An increase in gas flowrate reduces the gas mean residence time while increasing the solid residence time [1]. This makes a cyclone reactor especially interesting for application involving gas-solid reactions with undesired secondary reactions of the gaseous products, for example in flash pyrolysis.

Extensive research has been carried out for cyclone separators. However, despite the various application of cyclone reactors in industry, the literature on the subject is scarce.

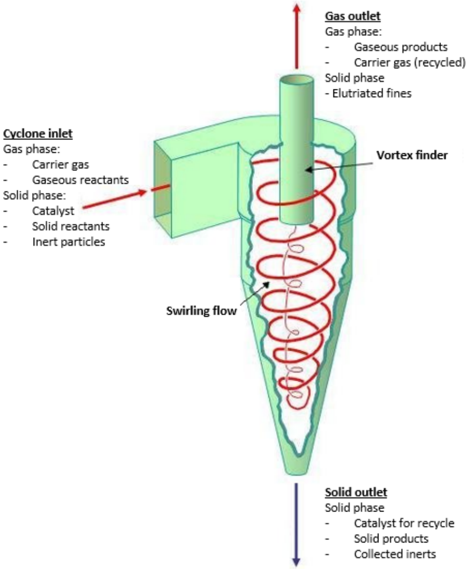

Figure 56: Cyclone reactor principle for gas solid systems

Specific objectives

The main objectives of the PhD project is:

- To study the important phenomena, such as gas phase mass transfer, mixing and gas-solid interactions in cyclone reactors.
- To develop improved reactor models for design and optimization of cyclone reactors.

Methods

The gas phase mixing in cyclone reactors, is investigated using selective non-catalytic reduction (SNCR) as a model reaction with a known kinetic model. A simple global reaction mechanism is shown below [2], to give an overview of the process.

$$4\,\mathrm{NO} + 4\,\mathrm{NH} + \mathrm{O_2} \rightarrow 4\,\mathrm{N_2} + 6\,\mathrm{H_2O}$$

$$4\,\mathrm{NH_3} + 5\,\mathrm{O_2} \rightarrow 4\,\mathrm{NO} + 6\,\mathrm{H_2O}$$

This is an existing application widely used in industrial combustion plants such as circulating fluidized bed boilers etc. giving the results a direct industrial relevance and comparison.

Pilot-scale experiments measuring the overall SNCR performance, the internal NO and ammonia concentration profiles have been conducted using the setup illustrated in Figure 2. The setup was built here at DTU and have modified as part of the PhD project. A different operational conditions, have been investigated, including, inlet temperature, gas velocity, reactant concentrations and particle feeding rates.

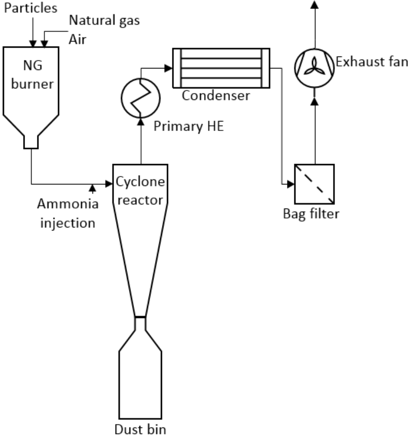

Figure 57: Overview of Cyclone reactor pilot setup

Furthermore, industrial scale measurements of SNCR in cyclone reactor have been performed at an industrial partners plant.

Different reactor models from the literature is used to simulate the experimental data using both simple and detailed reaction kinetics. Furthermore, a novel reactor network model have been developed for modeling the internal concentration profiles using detailed kinetics.

Results and Discussion

Interpretation of both modeling results and measurement data and the differences between them, can give insight into the cyclone mixing patterns and their effect on the reactors conversion efficiency. This is used to develop more complex but realistic models and give answers on how to more effectively utilize cyclone reactors.

Figure 3 shows an example of simple outlet measurements compared with the results from the simple models for cyclone reactors available in literature. This clearly shows that non of the existing models can reproduce both the conversion of NO and NH_3 with sufficient accuracy.

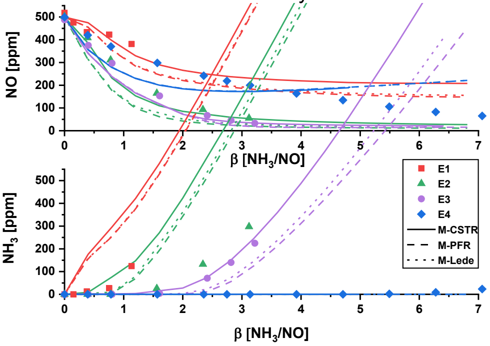

Figure 58: Pilot scale experimental results for and kinetic modeling results int. With varying inlet temperatures and ammonia dosing rate.

A new reactor network model has been developed using the gathered experimental data as well as literature data, while additional experimental work focusing on the influence of particles continues in parallel.

Conclusions

A pilot scale cyclone reactor setup for studying SNCR reactions and cyclone reactor properties, has modified and used to measure the effect of various operation conditions on the reactor performance, as well as the internal mixing and reaction behavior. Industrial scale measurements of and SNCR cyclone reactor have been carried out. The data collected from both pilot scale and industrial scale measurements have been used to evaluate existing models and develop a new reactor model.

Future work

The steps to follow in the future are:

- Complete solid loading studies
- Update modeling work with solid loading results
- Publish papers in progress
- Finalize PhD thesis

Acknowledgements

The research is carried out at the Center for Combustion and Harmful Emission Control (CHEC). The author would like to thank the Department of Chemical and Biochemical Engineering for funding this study.

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Novel Catalysts for the Selective Oxidation of Methanol to Formaldehyde

(November 2017- October 2020)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Catalysis is the science of making reactions happen under milder conditions and promoting specific products. Improvements in selectivity and activity can lower the material loss to unfavorable byproducts, and decrease the energy usage. Formaldehyde is a major chemical made from catalytic oxidation of methanol. In this process, specific challenges are fast catalyst deactivation and increasing power usage from gas blowers due to deposition of (toxic) Mo in the end of the catalyst bed. The development of novel materials may help decrease the power and Mo usage.

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Abstract

Novel Mo containing catalysts for the selective oxidation of methanol to formaldehyde have been synthesized, tested for catalytic activity and selectivity, and characterized by various methods including XRD, Raman and SEM. Tests of the catalysts have been performed at 250-400°C for up to 600 h on stream. Most promising were MoO_3 supported on Ca hydroxyapatite (HAP) and the Sr analogue. Industrial sized pellets were prepared for MoO_3/HAP, which elucidated that diffusion aspects must be taken into account going from powder to pellets.

Introduction

Formaldehyde is the most significant aldehyde commercially available as it is an irreplaceable C_1 building block for higher-valued products due to its high reactivity [1]. The annual global production of formaldehyde is expected to increase with a CAGR of 4.8-5.8% and reach a market of 36.6 million tons by 2026 [2,3]. Formaldehyde is mainly produced through either the silver process or the Formox process [1].

In the Formox process, the formaldehyde is formed by catalytic oxidation of methanol over an iron molybdate catalyst ($MoO_3/Fe_2(MoO_4)_3$), which a-chieve high selectivities (92-95%) at high conversions (>99%) [1]. The catalyst, however, is not stable during reactions conditions due to formation of volatile molybdenum compounds [4]. It is thus of interest to develop novel, more stable catalysts for the oxidation of methanol to formaldehyde.

Specific Objectives

The overall objective of the PhD project is to investigate and develop new catalysts for the selective oxidation of methanol to formaldehyde. This was done through the following parts.

Part 1: To make an extensive investigation of promissing materials in the existing literature.
Part 2: Testing of alkali earth metal molybdates as catalysts for the selective oxidation of methanol to formaldehyde.
Part 3: Investigation of MoO_3 supported on hydroxyapatite and the Sr analogue by catalytic testing and various characterization methods.

Experimental

Catalytic samples were prepared by various methods such as co-precipitation, reflux, sol-gel synthesis and incipient wetness impregnation. The samples were characterized by XRD, N_2-physisorption, ICP, NH_3-TPD, CO_2-TPD, TPR, SEM, STEM, Hg-porosimetry and Raman spectroscopy. Catalytic tests have been performed on a lab scale, fixed bed reactor setup (described in [5]) at temperatures from 250-400°C. Methanol feeding was achieved by saturating the gas mixture in a bubble flask before entering the reactor. The effluent was analyzed for CH_2O, methanol, dimethyl ether, di-methoxymethane, methyl formate, CO and CO_2 by using a GC with both TCD and FID detectors.

Results and Discussion

Various samples of alkali earth metal molybdates ($MMoO_4$, M = Mg, Ca, Sr, Ba) were synthesized and tested (Figure 1) and was found to have good selectivity and activity when prepared with excess Mo, however, it was found by Raman spectroscopy that the excess Mo disappeared under operation, which could also be seen by decreasing activity and selectivity over time. If instead MoO_3 was impregnated on an apatite support such as $(Ca_5(OH)(PO_4)_3$ or $Sr_5(OH)(PO_4)_3)$ $CaMoO_4$ and $SrMoO_4$ was also observed by XRD after calcination, but much less Mo have been used compared to bulk $MMoO_4$ and $Fe_2(MoO_4)_3$. It was found by SEM (Figure 2), that the $CaMoO_4$ was formed as small particles on the surface of the large support particles. These catalysts have better selectivity, activity and stability, even though crystalline MoO_3 was not measureable by XRD. The selectivity stayed above 89% for over 400 h on stream for a powder test (Figure 3). When testing the catalysts in the form of industrial sized pellets it was found that there is a large dependence on the pellet density (Figure 4) of both selectivity and activity. This is due to diffusion limitations, which must be taken into account when developing an industrial catalyst.

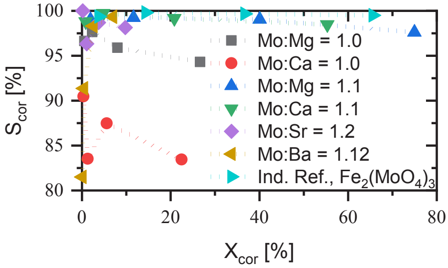

Figure 1: Reversible byproducts corrected selectivity towards formaldehyde vs. the corrected conversion obtained by measurements at 250°C, 300°C, 350°C and 400°C. 25 mg catalyst (150-250 µm) diluted in 150 mg SiC. Flow: 150 NmL/min, $MeOH/O_2/N_2$ = 5/10/85 %

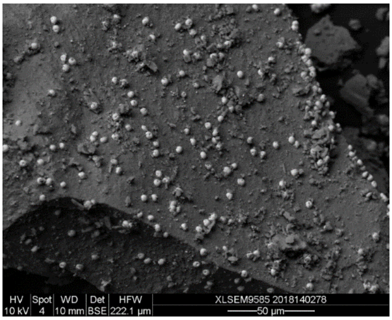

Figure 2: SEM image of fresh 10 wt% MoO_3/HAP.

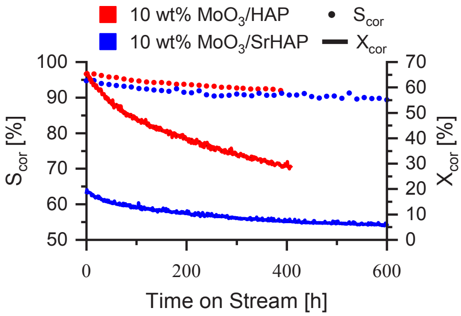

Figure 3: Reversible byproduct corrected selectivity and conversion vs. time on stream. 25 mg catalyst (150-250 µm) diluted in 150 mg SiC at 350°C. Flow: 150 NmL/min, $MeOH/O_2/N_2$ = 5/10/85 %.

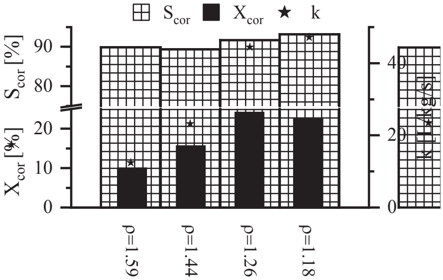

Figure 4: Reversible byproduct corrected selectivity, conversion and 1st order rate constant as function of pellet density (ρ) in g/cm³ at 350°C for MoO_3/HAP. 1 pellet (60-91 mg). Flow: 300 NmL/min, 5% MeOH, 10% O_2 and 85% N_2.

Conclusions

It has been found that excess Mo on alkali earth metal molybdates give high selectivity and activity but evaporates during operation. MoO_3 impregnated on hydroxyapatite and the Sr analogue gives selective catalysts for the oxidation of methanol to formaldehyde with good stability. The pellet density have a significant influence on the activity and selectivity of MoO_3/hydroxyapatite catalysts.

Acknowledgements

This project is part a collaboration between the CHEC research center at Department of Chemical and Biochemical Engineering at DTU and Haldor Topsøe A/S. Funding from Independent Research Fund Denmark (DFF – 4184-00336) is gratefully acknowledged.

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Theory, Simulation and Models for Electrolyte Systems with Focus on Ionic Liquids

(March 2018 – March 2021)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

Electrolytes are indispensable elements in energy storage since the positive and negative electrodes are interconnected by an electrolyte solution that determines the charge transport during the charge/discharge process. Ideal electrolytes should fulfill the following requirements: *i.e.,* wide voltage window, excellent electrochemical stability, high conductivity, high ionic concentration, environmental friendliness. The design of electrolytes with simulations, theories and models for a good performance is helpful to guide the synthesis of electrolytes, so as to realize the efficient use of energy.

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Abstract

It is expected that the use of ionic liquids (ILs) in electrolyte solutions for the new-generation lithium ion batteries will greatly enhance the safety and energy storage capacity. Fundamental molecular insights are useful for understanding the advantages IL solvents over organic ones. In this project, in order to deeply understand the molecular mechanism of the ILs based electrolytes. A series of model IL electrolytes with high electrochemical properties will be developed. The structures that affect the properties of electrolytes will be investigated. The suitable ILs will be screened and designed to guide the experiment and application.

Introduction

Lithium-based battery, as opposed to traditional alkaline battery, has emerged as a novel rechargeable energy storage device due to its high charge density and low self-discharge.[1,2] Technically, lithium-ion battery utilizes the transportations of lithium ions from the negative electrode to the positive electrode in organic solvent electrolytes to achieve the charging/discharge process. Thus far, most of studies on the development of high-performance lithium-ion battery still involve the uses of organic solvent electrolytes, such as propylene carbonate, diethyl carbonate, and dimethyl carbonate [refs]. However, the uses of organic solvent electrolyte in the lithium-ion battery exist two flaws: (i) the inevitable chemical reactions within the electrolyte decrease battery lifetime and (ii) the high inflammability of organic substances increases the risk of fire or explosion. Therefore, developing safe and sustainable novel electrolytes for the lithium-ion battery is a crucial challenge in current energy storage industry.

An ionic liquids (IL), an environmentally-friendly green solvent, is an alternative to traditional organic solvent in battery manufacturing industry, because of its unique physicochemical properties, such as high thermal stability, negligible vapor pressure (i.e., neither flammable nor volatile), and high ionic conductivity. An IL is a molten salt in the liquid state at room temperature, which exists a large number of free cations/anions and short-lived ion pairs. Generally, when using an IL as solvent to dissolve the lithium salt, the free IL ions are easy to associate with the Li+ through ionic coupling interactions.

To enhance the electrochemical performance of lithium-ion battery, it is necessary to examine the solvation behaviors of lithium salt in varied electrolyte solutions. Fundamental molecular insights are useful for understanding the advantages of novel IL solvent electrolytes over traditional organic solvent electrolytes. Therefore, in this project, two organic solvents (DMC and DEC) and four IL solvents ($[C_nmim][BF_4]$ and $[C_nmim][TFSI]$ (n=2, 4)) were firstly computationally studied to examine the physicochemical properties of the high concentration electrolytes.

Research Progress of Project

1. Model development of electrolyte system

The simulation system is constructed with 50 Li^+, 50 $TFSI^-$ and 135 DMC or 94 DEC for organic solvents, and 75 $[C_2mim][BF_4]$ or 61 $[C_4mim][BF_4]$ or 45 $[C_2mim][TFSI]$ or 39 $[C_4mim][TFSI]$ for ILs, respectively that keep a consistent salt concentration (2mol/L) in this simulation. The system is in a cubic box with a dimension of 50 Å in length, width and height and sketched in Fig 1.

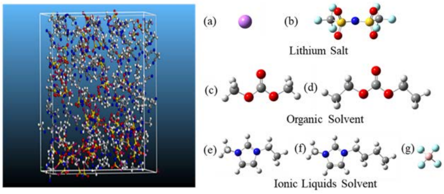

Figure 1. Structures of the ions and solvent molecules involved in our MD simulations: (a) lithium (Li^+); (b) [bis(trifluoromethanesulfonyl)imide] ($TFSI^-$); (c) dimethyl carbonate (DMC); (d) diethyl carbonate (DEC); (e) 1-ethyl-3-methylimidazolium ($[C_2mim]^+$); (f) 1-butyl-3-methylimidazolium ($[C_4mim]^+$); (g) tetrafluoroborate ($[BF_4]^-$).

2. Simulation details

All molecular dynamic simulations were performed with the Gromacs software. The general Amber force field was used to describe the atom types for DMC, DEC, $[C_nmim]^+$, $[BF_4]^-$, $TFSI^-$, and all-atom optimized potential for liquid simulations force field was used to describe Li^+ ions. Each simulation system is relaxed in the canonical (NVT) ensemble for the first 5ns and then in the isothermal-isobaric (NPT) ensemble for the next 5ns. Production simulation is carried out for 30ns in the NPT ensemble and for 10 ns in the microcanonical (NVE) ensemble to achieve the configurational equilibria. The Verlet algorithm with a time step of 1.0 fs is employed to integrate Newton's equations of motion. During the simulation, the trajectories are recorded at every 0.1ps for further post-analysis.

3. Physicochemical properties

The density and viscosity of both the LiTFSI-organic solvent and LiTFSI-ILs solvent electrolytes at 298K (Table 1) were firstly calculated. It is seen that the computed density and viscosity of the LiTFSI-ILs solvent electrolytes are higher than that of the LiTFSI-organic solvent electrolytes at 298K. Additionally, for the ILs solvent electrolytes with the common anion ($[BF_4]^-$ or $[TFSI]^-$), we observed that both the density and viscosity of $[C_2mim]$-type electrolytes is a little higher than $[C_4mim]$-type electrolytes, indicating that the physicochemical properties of the $[C_nmim]$-type ILs solvent electrolytes is affected by the chain length n of cyclic carbonate. Meanwhile, the total conductivity of the six electrolytes at 298K were calculated. Simulation results revealed that the four ILs solvents exhibit a notable higher ionic conductivity than the two organic solvents, implying that solvents with ionic structure have higher conductivity than molecular structure.

Table 1. Density (unit: g/cm^3), viscosity (unit: kg/m·s) and conductivity (unit: S/m) for the LiTFSI-organic and LiTFSI-ILs solvent electrolytes at 298K.

Property	DMC	DEC	$[C_2mim][TFSI]$	$[C_2mim][BF_4]$	$[C_4mim][TFSI]$	$[C_4mim][BF_4]$
Density	1.47	1.37	1.74	1.53	1.67	1.42
Viscosity	0.39	0.94	1.92	1.55	1.03	1.53
Conductivity	2.19	1.57	2.74	4.26	5.07	5.59

4. Microstructural analysis

In order to explore the relationship between the structure and properties of electrolyte, the electrolyte solvation of the cation Li+ was discussed in the organic and ILs solvents to reveal the solution interactions between solute and solvent by radial distribution function (RDF),

$$g(\mathrm{r}) = \frac{\langle \sum_{i,j} \delta(r-r_{ij}) \rangle}{N\rho} \qquad (1),$$

where N is the number of particles, ρ is the number density, r_{ij} is the spatial distance.

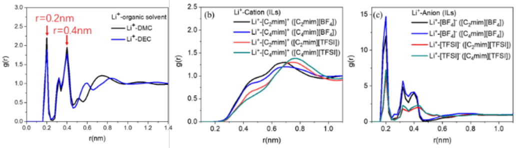

Figure 2. Composite graph of the radial distribution functions representing the spatial correlations of the cation Li^+ with (a) the two organic solvent molecules, and with the (b) cations and (c) anions of the four ILs solvents at 298K.

5. Conclusion

In this work, MD simulations were employed to investigate the solvation behaviors of the lithium salt LiTFSI in two organic solvent and four ILs solvent electrolytes. Simulation results revealed that the LiTFSI-ILs solvent electrolytes have higher density and viscosity, and larger conductivity than the LiTFSI-organics solvent electrolytes in high concentration solutions. Meanwhile, the cation Li^+ has strong interactions with the anion TFSI- through coordinating with the O(TFSI) atom, not the more electronegative N(TFSI) atom. More important, the organic solvents restrict the free motion of the anion $TFSI^-$, while the ILs solvents facilitate the ionic association of the $TFSI^-$-$TFSI^-$, causing a high conductivity for the ILs-based electrolytes.

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Incorporating Polyrotaxane Materials in Dielectric Elastomer Actuators

(December 2018- December 2021)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Contribution to the UN Sustainable Development Goals

The development of commercially viable dielectric elastomer actuators will allow for the creation of a new class of lightweight and flexible electromechanical actuators. The application of such linear actuators range from consumer electronics to soft robotics and prosthetics creating new and efficient technical solutions that can not be achieved with traditional actuators. The rise of this innovative technology would bring with it a completely new type of mechanical drivers that could mimic biological muscles in their function and form.

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Abstract

Polyrotaxane materials can be used as a novel type of cross-linkers for the preparation of slide-ring elastomers. These elastomeric networks have freely sliding cross-links that imbue the material with numerous desirable mechanical properties for dielectric elastomer actuators. However, chemical modification of the polyrotaxanes is still necessary before they can be incorporated into elastomeric networks due to their low miscibility with common elastomer precursors. Here, a synthetic pathway has been proposed to increase the compatibility of polyrotaxane cross-linkers and polysiloxanes in order to prepare silicone slide-ring elastomers.

Introduction

Polyrotaxane materials composed of threaded molecular rings can be assembled into a novel type of elastomeric material that has moving cross-linking points instead of the stationary cross-linking points seen in conventional networks [1]. These sliding cross-links impart unique mechanical properties due to a molecular scale phenomenon caused by the sliding entropy that is commonly described as the pulley effect. When a force is applied to the material, the sliding cross-links dissipate stress throughout the material in a similar manner to a rope and pulley. This allows for the design of softer elastomers with higher strains at break [2]. Additionally, the sliding elastomers have been shown to exhibit low hysteresis during cyclic loading which has been attributed to the air-spring like behavior of the threaded cyclic rings [3]. The two phenomena are illustrated in Figure 1.

These mechanical properties are desirable for dielectric elastomer actuators (DEAs) where softer materials enable higher degrees of actuation and where low hysteresis is necessary for their energy efficient operation. It is thus of interest to incorporate polyrotaxane cross-linkers to existing polysiloxane based DEA platforms. In the current project we have proposed a synthetic pathway to create polyrotaxane cross-linkers based on polyethylene glycol (PEG) and α-cyclodextrin (α-CD) that contain vinyl groups allowing them to be incorporated into polysiloxane networks through hydrosilylation. This type of curing chemistry is commonly used in silicone elastomers due to its high efficiency and selectivity [4].

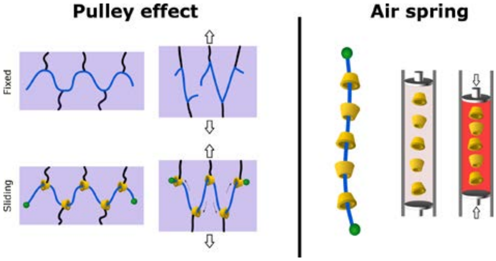
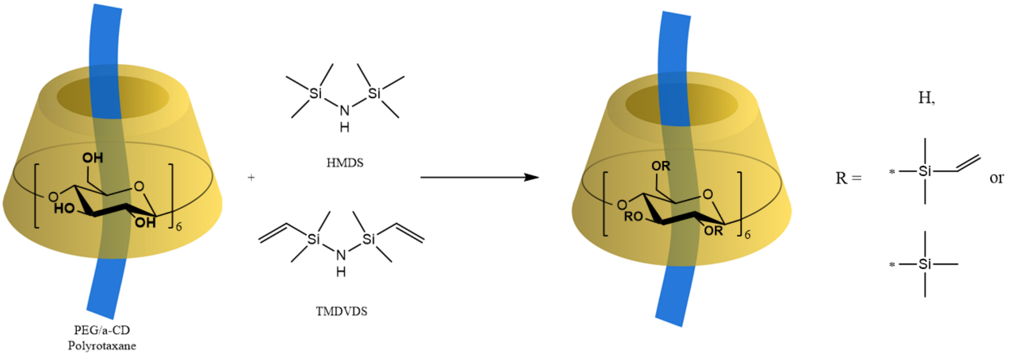


Figure 1: Pulley effect and air spring behavior

Results and Discussion

Two silylation agents were utilized to substitute the hydroxyl groups on the threaded α-CD rings as shown in Scheme 1. Tetramethyldivinyldisilazane



Scheme 1: Substitution of the hydroxyl groups on threaded a-CD rings.

(TMDVDS) was used to introduce the vinyl functional groups necessary for hydrosilylation. The addition of hexamethyldisilazane (HMDS) was necessary to control the amount of vinyl functional groups per α-CD ring without compromising the degree of substitution. Control over the vinyl content of the modified polyrotaxanes is essential to avoid multiple static cross-linking points forming on a single α-CD ring. A high degree of substitution, however, is necessary to disrupt the packing structure of the threaded rings and to increase the miscibility between the polyrotaxanes and the polysiloxane precursors.

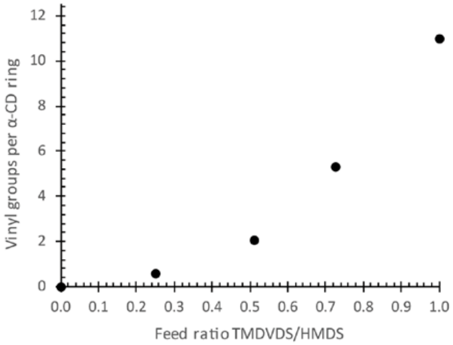


Figure 2: Vinyl groups per α-CD ring based on the feed ratio

Figure 2 shows how the vinyl content per α-CD ring can be tuned by the feed ratio of (TMDVDS) and (HMDS). The degree of substitution stayed stable at around 2.4. The modified polyrotaxanes were soluble in toluene, tetrahydrofuran and chloroform.

Conclusions

A mixture of TMDVDS and HDMS can be used to create modified polyrotaxane cross-linkers containing the functional groups necessary for hydrosilylation. The modified polyrotaxanes are also soluble in solvents commonly used for linear polysiloxanes, which would potentially allow them to be dissolved and mixed with silicone precursors.

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Field Concentration in Hydrogel Elastomer Devices

(July 2017- July 2020)

Contribution to the UN Sustainable Development Goals

Modern technologies are aiming for soft, shapeable and thin flexible devices. Dielectric elastomer actuators (DEAs) consisting of an elastomer with compliant electrodes are excellent candidates for making these types of devices. However, development of DEAs is often complicated due to incompatibility of elastomer and electrodes. Therefore, novel electrodes based on hydrogels are developed to address the challenges and improve the overall actuator performance. This research will lead to increased knowledge on soft electronics, which can be integrated in medical applications and in everyday life.

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Abstract

In this work, experimental observations associated with electric field concentration along the edges of the hydrogel-elastomer actuators are reported. The investigated actuators comprise a dielectric elastomer and conductive hydrogels as compliant electrodes. Experiments showed that the dielectric breakdown usually occurs at the edges of the hydrogel electrodes. Before the elastomer breaks down, different instability phenomena are observed, such as salting out, localized heating, and plasma formation along the edges of the hydrogel. Plasma, created by the breakdown of air, causes localized heating while simultaneously reducing the electrical field concentration, and in this way, it protects the given device from breaking down electrically. The significance of these observations is discussed.

Introduction

Here the reported hydrogel elastomer devices are dielectric elastomer actuators (DEAs). DEAs are built by sandwiching a dielectric elastomer between two compliant electrodes. When a voltage is applied to the electrodes, charges build up on two opposing sides of the elastomer and the device decreases in thickness and expands in area [1]. This simple movement is called electromechanical actuation and can be employed when fabricating artificial muscles, soft robotics and stretchable electronics [2].

Many different types of electrodes have been applied in the DEA systems. One of the most recent types is made of hydrogels. Use of hydrogel as an electrode enables fabrication of many novel devices, such as transparent loudspeakers, transparent artificial muscles or sensors [3]. A hydrogel is a hydrophilic polymer network swollen in water. These materials are freestanding, stretchable, and transparent. Hydrogels become electrically conductive upon incorporation of ions (e.g. from inorganic salts) thus enabling their use as transparent electrodes in dielectric actuators [4].

In this work, each investigated actuator is made by sandwiching a dielectric silicone elastomer film between two hydrogels. Subsequently, cyclic voltage with predefined amplitude and frequency is applied until the device breaks down electrically. Dielectric breakdown occurs when the elastomer cannot withstand the electric field that it is subjected to. After the breakdown DEA cannot function anymore [5].

In this work, several observations on the field concentration along the edges of hydrogel are reported. When the voltage is applied, before the elastomer breaks down, optical changes in the DEA are observed. The significance of these observations is discussed.

Results and Discussion

The preparation of the DEA devices is schematically presented in Fig. 1. The dielectric elastomer film is pre-stretched and fastened onto a rigid frame. Two circular hydrogel membranes are attached on both sides of the elastomer and are connected to a power supply (Fig. 1a, b). The ensemble of elastomer and hydrogel is transparent (Fig. 1c). Fig. 1b presents how the electric field is distributed when the voltage is applied to the device. The electric field lines are perpendicular to the surface of the conductors. Electric field lines are concentrated and curved at the edges of the hydrogel.

The investigation of the long-term performance of the dielectric actuators did not yield any conclusive information about robustness of the studied devices. However, it has been observed that most of the samples break down near the edge of the electrode, which indicates that field is concentrated on the edges.

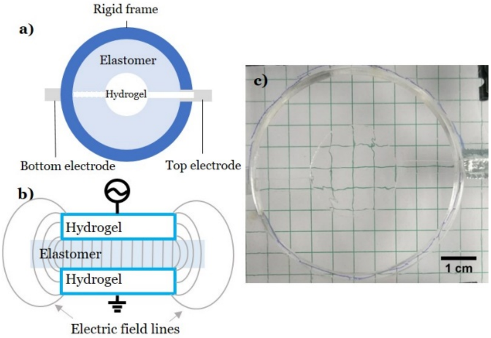

Figure 59: DEA set up. a) Schematic top view of a device. b) Schematic side view of a device. c) A photo of a transparent device.

After multiple actuation cycles salt precipitates out on the surface of the hydrogel (Fig. 2a). This phenomenon is called salting out and is caused by local temperature increase along the edges of the electrode (Fig. 2b). Before the experiment, salt is dissolved fully in the hydrogel and device is transparent. When the sinusoidal voltage (frequency 1 kHz and amplitude 10680 V) is applied, certain areas of the hydrogel start turning white after around 5 minutes of experiment, due to salt precipitation. After 10 minutes the salting out becomes even more pronounced. Generally, it is observed that higher frequencies and amplitudes of the applied voltage lead to higher local temperatures and thus results in a more intense salting out. If the device is turned off and kept for 1 hour at ambient conditions, the salt absorbs humidity from the air and re-dissolves. Thereby the device becomes fully transparent again.

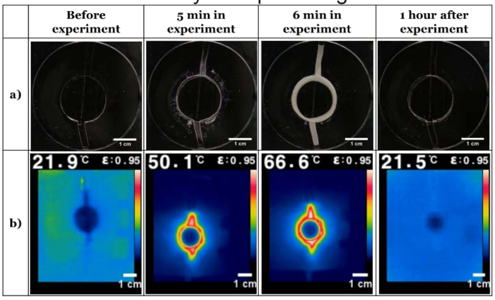

Figure 60. Salting out and localized heating. a) The evolution of the salting out process before experiment, 5 min in experiment, 10 min in experiment and after experiment. b) Corresponding thermal images.

When the experiment is performed in a dark room, purple light along the edges of the electrode can be observed (Fig. 3 b). The dielectric breakdown strength of the air is much lower than that of the elastomer. Due to the electric field concentration around the edges, air starts to break down while the elastomer remains intact (Fig. 3a). The breakdown of air is generating plasma, which heats up the surrounding air and causes salting out.

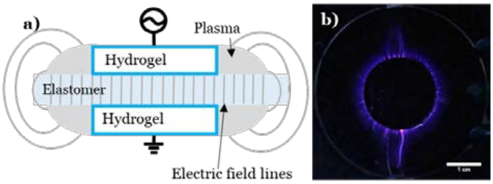

Figure 61: Hydrogel plasma. a) Schematic of a device. b) A plasma of purple light along the edges of the hydrogels.

Conclusion

In this work, the electric field concentration in hydrogel-elastomer actuators is studied. The devices are mainly breaking down along the edges of the hydrogels due to higher electric field concentration in these zones. Before the elastomer in a device breaks down, the concentrated field causes the air to break down. This leads to formation of plasma, local temperature increase, and hydrogel salting out. Plasma protects the device from breaking down by dissipating energy into the air and reducing the field concentration. The field concentration of hydrogel elastomer devices can be used for tissue engineering or electroluminescent displays [6].

Acknowledgements

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Conceptual Design of Biorefineries for the Synthesis of Sustainable Value Chains

(November 2018 - October 2021)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Contribution to the UN Sustainable Development Goals

Developing countries have a great industrialization potential within agroindustry. By utilizing the agricultural wastes as feedstock for an integrated biorefinery to produce biofuels, platform chemicals and energy, this potential augments. This complies with the concept of circular and thus sustainable value chains and promotes sustainable economic growth, independent from fossil resources. This work aims to synthesize such value chains in a conceptual manner to exploit this potential and to increase human development in these countries.

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Abstract

The scope of this work comprises the development of a digital twin for a biorefinery by the application of Process Systems Engineering techniques. In the first stage, the objective is to determine an optimal process design by superstructure optimization. With the optimal process design, the operation of the process is optimized by increasing the productivity through process integration and intensification, as well as an optimal scheduling of the process. Lastly, varying feedstock supply, as well as fluctuating availability and demand are considered and assessed regarding their robustness in order to yield a sustainable value chain.

Introduction

The majority of today's commodities, as fuels, plastics, cosmetics and many more are produced from fossil feedstocks in chemical processes. One of the major challenges for this industry is to successfully replace traditional processes by more sustainable alternatives [1]. This will radically change global value chains in the process industry. In order to reduce the global CO_2 emissions, both the feedstock has to be renewable and the process should generate as little CO_2 as possible.

In this industrial transformation, the biorefinery concept plays a key role: here, for example agricultural waste is used as feedstock and processed by chemical or biotechnological processes towards multiple, value-added products [2]. However, the economic potential of such biorefineries is critical and as of today not fully exploited. The resulting question here is to find combinations of products to be produced from a certain feedstock in order to yield an economically robust value-chain. In order to do so, the design of these biorefinery processes has to be performed conceptually [3]. Hence, a three-stage Process Systems Engineering approach is followed. The fully implemented approach is the equivalent to a digital twin of a biorefinery. The approach and its outputs are explained in the following sections.

Specific Objectives

Process Design Stage

The first stage of the approach and of the PhD project is the project design stage with the objective of achieving an optimal process design. The design of a base-case process is based on a single feedstock, in this case wheat straw, and one fixed product, xylitol, a sugar substitute with many beneficial health properties, especially suitable for diabetic nutrition [4]. Further value-added products are to be specified in order to extend the base-case design. Possible products are for example succinic acid, lactic acid, bioethanol, sustainable aviation fuels or others.

Figure 1: Feedstock Wheat Straw and possible product xylitol

Xylitol can be produced biotechnologically in a microbial fermentation process, which requires sugars. Wheat straw is an agricultural waste containing many different sugars in polymeric form. In order to obtain monomeric sugars, the biomass is pretreated. After using some of the sugars for the fermentation towards xylitol, it is recovered in a suitable downstream process.

In order to design this process, for every mentioned unit operation, mechanistic models are developed, with the pretreatment, the fermentation and an evaporation and a crystallization unit in the downstream processing as main components. Both are calibrated with experimental and literature data and assessed by uncertainty and sensitivity analyses towards their robustness and ability to be utilized for process design.

The models are connected in a so-called superstructure, which can be optimized yielding the best combination of unit operations and their size for a given capacity as optimal process design. This is an iterative process, so other models for alternative unit operations and process trains for the other sugars and components in the feedstock can be included to find an overall optimal design.

Process Optimization Stage

In the next step, the optimal design is taken into the process optimization stage, where the objective is to find an optimal operation strategy for the process. This involves several lines of investigation, as for example the best operation mode for the fermentation processes. Closely connected are design decisions as e.g. the number of parallel unit operations, which have to be scheduled optimally.
Other tasks in this stage involve Process Integration and Intensification in order to increase the productivity, as well as to reduce the amount of generated waste. Elaborating solutions for the mentioned tasks yields an optimal operation.

Value Chain Optimization Stage

With the optimal process design and operation, the third stage is entered, where the focus lies on the technological and economic analysis of the utilization of different feedstocks. This is motivated by the fact, that there is a geographically dependent availability of feedstocks and a fluctuating feedstock availability on the market [5].

Hence, the optimal value chain represents a cheap feedstock, which is processed to several value-adding products with high productivities for this respective feedstock. In order to ensure the economic resilience of this value chain, scenario analyses are performed. Analyzing different capacities and different economic uncertainties will then yield a robust solution. Furthermore, ecologic assessments will indicate the potential for increasing sustainability. By concluding the third stage, the result then is a value chain, which is both economically viable and sustainable. Moreover, the developed framework is the finished digital twin.

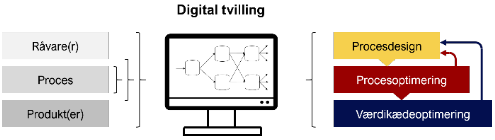

Figure 2: Schematic representation of the digital twin

Results and Conclusions

Referring back to the entrance statement regarding the Sustainable Development Goal Number 9 it is now possible to assess possible implementations of a biorefinery in a developing country. Taking the Philippines as example, one of the most abundant feedstocks is rice straw [6]. Furthermore, a high percentage of the population suffers from type 2 diabetes, indicating a high potential for an emerging sugar substitute market to sell xylitol there [7].

With the digital twin, possible value chains can be designed, assisting decision-making for companies or other entities on building a biorefinery, producing xylitol and other value-adding products with rice-straw as feedstock. This highly supports the economic growth in developing countries, tackling especially structural deficits, by designing locally implementable solutions. This then will contribute to the transition in the process industry for a globally more sustainable future.

Acknowledgements

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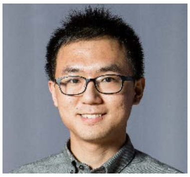
Coating interlayer adhesion loss

(September 2017- August 2020)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

It is common practice to apply organic coatings on metallic substrates to prevent corrosion and obtain a pleasing aesthetic appearance. Weak interlayer adhesion can cause a coating system to fail, which significantly minimizes their service life. This project focuses on the study of the mechanisms of the adhesion loss and the strategies to improve intercoat adhesion. Maximizing the service time of coating systems reduce chemical consumption, contributing to sustainable development.



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Abstract

Weak interlayer adhesion between an epoxy primer and a polyurethane (PU) topcoat can result from improper curing of the PU topcoat under low ventilation or suppressed ventilation conditions. In this work, the curing process of PU under different ventilation conditions was studied. The increase in air velocity leads to the reduction of residual solvent, but has limited effect on the curing reaction. Under low air velocity conditions, the final hardness of the PU coating is reduced due to a higher retention of solvent and its plasticizing effect.

Introduction

Corrosion protection of steel structures, such as ships, wind turbines, bridges and oil rigs, is almost exclusively done by the use of anticorrosive coating systems [1]. This multilayer coating system typically consists of a primer such as an epoxy primer, directly in contact with the steel substrate, followed by an intermediate epoxy coating to build up a substantial protective coating thickness. Finally, a top coat of PU is applied for protection against Sunlight and to provide an aesthetically pleasing surface. Such coating systems can, in many cases, provide corrosion protection for more than 20 years. One of the causes that can lead of a failure and reduce the service life of such systems is a weak interlayer adhesion. When the interlayer adhesion is weak it can lead to the detachment of the top coat from the remaining coating system. In this project, the underlying mechanisms of interlayer adhesion loss will be investigated.

The weak adhesion of the PU topcoat to the underlying epoxy coating can occur under evaporation-suppressed conditions. The adhesion between the PU topcoat and the epoxy primer is not sufficient, leading to a situation where the topcoat becomes easy to remove. The evaporation-suppressed conditions slow the evaporation of solvents, trapping them inside the still soft coating system. In addition, for short overcoat intervals, some molecules in the epoxy primer may migrate into the PU topcoat. This might induce improper curing of PU topcoat aggravating the problem.

Specific objectives

The focus of the project will be to investigate the mechanisms of interlayer adhesion loss. The first goal is to study the curing process of a PU coating and the parameters influencing it. The second goal is to improve the hardness development of the PU topcoat and its adhesion even if the epoxy-PU system is cured in evaporation-suppressed conditions.

Results and discussion

The effect of air velocities on the hardness development of a solvent-based thermoset PU coating was studied. The PU films were applied on a glass panel by drawdown application using a Baker film applicator with a gap of 200 μm and a width of 80 mm. The films were dried in a drying cabinet, provided by DAVENKA A/S. The air velocity inside the drying cabinet can be controlled(low, medium and high) while the temperature was constant at 25.0 ℃. The solvent evaporation rate was followed gravimetrically, the curing monitored by the use of attenuated total reflectance (ATR)-FTIR and the coating hardness measured using the pendulum method. Figure 1 shows the results of the curing of PU films under the conditions of different air velocities.

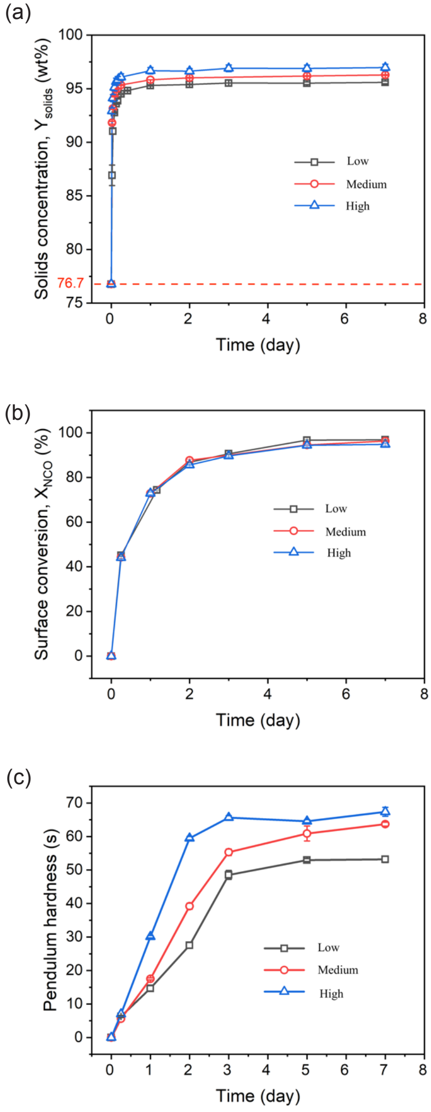

Figure 1: Curing of PU films under the curing conditions of different air velocities: (a) The increase of solids during solvent evaporation. The red break line shows the solids concentration of the PU formulation. (b) The conversion of isocyanate groups in the coating, and (c) The hardness development of the coating. The standard deviation is shown with error bars in all three plots.

In Figure 1(a), it can be seen that the evaporation of solvent of the PU films under different ventilation conditions follows the same trend with a fast evaporation rate in the first six hours and a much slower rate afterwards. It can be seen that the solids concentration is lower as the air speed decreases, meaning that more solvent is trapped inside the PU film. In Figure 1(b), the curing reaction rate is fast within the first day and then gradually slows down. The surface reaction rate of isocyanate under different air velocities shows no clear difference, suggesting that the air velocity impact on the curing of PU films is not relevant. Looking at Figure 1(c), the pendulum hardness of PU films increases rapidly during the first three days, that corresponds to approximately an 85% of the curing process according to 1(b). The hardness development of the PU films becomes slower after three days. The correlation between the isocyanate reaction rate and the hardness of the PU, indicate that the later depends directly on the former with a set off determined by the amount of residual solvents trapped inside the film when the curing reaches a certain degree. The plasticizing effect of this residual solvent results in the softer PU films.

The increase in air velocity was observed to reduce residual solvent but has a limited effect on the drying time (see Figure 1(a)). However, the observed results are not in agreement with the simulation of Kiil [2] that developed a model to simulate the influence of wind velocity on the curing process of PU films. The simulations showed that a lower wind velocity caused longer drying times, but the final solvent retentions were practically the same. The reason is worth to be further explored in the future.

Conclusions

The increase in air velocity was found to reduce the solvent retention in PU films, thereby increasing their hardness. The cause of the disagreement with the simulation by Kiil [2] should be investigated in the future.

Acknowledgements

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Improvement of Mechanical Properties of Anisotropic Glassy Polystyrene

(June 2018 - May 2021)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Polymer gels and networks are widely used in our daily life. While permanent network can resist flow and creep but with limited processability and recyclability, physical networks are more processable and recyclable but creep at long time. The idea behind this project is to combine and control in double dynamic networks all distinct features that make them ideal for applications and prolong lifetime of polymer networks.

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Abstract

Glassy polystyrenes with highly oriented molecules (referred as anisotropic PS) have very high strength along the orientation direction but low strength perpendicular to the orientation direction. To improve the mechanical properties, carboxylic acid groups were introduced into the samples. Both linear viscoelastic (LVE) and non-linear extensional measurements suggest that hydrogen bonds are not formed above glass transition temperature, which facilitates the processing of anisotropic PS. The resulting acid-containing PS fibers have higher yield stress and ductility at room temperature compared to the non-modified ones.

Introduction

Polystyrene (PS) is a widely used thermoplastic polymer. It is a brittle, amorphous transparent material with a glass transition temperature (T_g) of around 100 °C. Its hardness, transparency and thermostability make it good candidate for commercial products. However, its brittleness limits the applications. Although flexibility of polystyrene can be achieved by mechanical rejuvenation [1], it is merely temporary with a time scale of hours. Recently a long-lasting (more than half year) flexible polystyrene was reported, achieved by stretching polystyrene melts at a rate faster than the inverse Rouse time and subsequently quenching below T_g. [2] The resulting highly oriented (anisotropic) polystyrene fibers have a much higher strength than isotropic polystyrene, making it suitable for strength and flexibility demand applications. However, these highly oriented polystyrene fibers are strong in the stretching direction, but relatively weak perpendicular to the stretching direction as result of reduced inter-chain interaction.

In order to improve the mechanical properties of the anisotropic polystyrene, in this work heat-labile reversible hydrogen bonding has been introduced into the material. Rheological behavior and mechanical properties of the modified polystyrene are studied.

Specific objectives

The effect of hydrogen bonds on mechanical properties is hardly studied for vitrified materials below T_g. The hydrogen bond exchange has a feature of temperature dependence. The purpose of this project is to make use of this feature to improve the performance of vitrified materials while maintaining the processability. By introducing a limited amount of hydrogen bonding sites in the form of carboxylic acid group along the chains, the inter-chain interaction is expected to increase in vitrified polystyrene, thus the strength perpendicular to the stretching direction is increased. At the same time, since hydrogen bond exchange is fast at high temperatures, processing in the melt state above T_g is expected to be unaffected.

Materials

Three different PS based materials were used:
- PS, molecular weight M_w=122k, T_g=100°C;
- $PS_{0.95}VBA_{0.05}$ (Copolymers of styrene [S] and 5% 4-vinylbenzoic acid [VBA]), M_w=113k, T_g=114°C;
- $PS_{0.91}VBA_{0.09}$, M_w=116k, T_g=122°C.

Results and Discussion

Rheology Linear viscoelastic measurement of PS, $PS_{0.95}VBA_{0.05}$ and $PS_{0.91}VBA_{0.09}$ are plotted in van

Gurp-Palmen-plot at the reference temperature of 150 °C as shown in Fig.1a. These master curves have a similar shape with a slight horizontal shift that is due to the T_g difference. The three normalized curves overlap in Fig.1b (normalized by the high-frequency crossover) indicate that the number of entanglements per chain is identical.[3] Since these polymers have comparable molar masses, the results suggest that the acid groups hardly form hydrogen bonds above T_g.

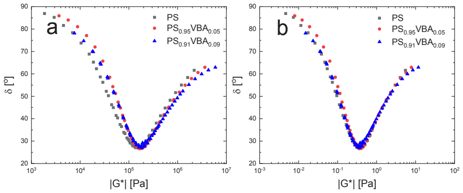

Fig.1 a) van Gurp-Palmen-plot built at 150°C, b) normalized van Gurp-Palmen-plot

Fig.2a compares the normalized non-linear extensional behavior of PS and $PS_{0.95}VBA_{0.05}$ measured at different equivalent rates. By increasing the stretch rate, the strain hardening effect, resulting from oriented and stretched polymer chains, is more evident. These two samples show similar extensional behavior at high temperature above T_g. Of particular interest are samples that have been stretched faster than the inverse Rouse time, which have the highest strain hardening. Fig.2b shows a direct comparison of PS, $PS_{0.95}VBA_{0.05}$ and $PS_{0.91}VBA_{0.09}$ stretched at equivalent rates faster than the inverse Rouse time. The high similarity of the strain hardening indicates that hydrogen bonding is not activated at non-equilibrium

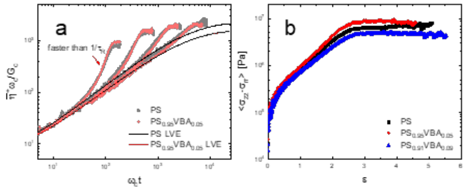

Fig.2 a) Comparison of normalized extensional stress growth coefficient for PS and $PS_{0.95}VBA_{0.05}$, b) Comparison stress as a function of Hencky strain at equivalent rate faster than inverse Rouse time for all three polymers

Mechanical properties All three polymer melts were stretched to Hencky strain 3.5 above T_g and quenched by rapid cooling to room temperature. The presence of acid dimers was confirmed by ATR-FTIR spectroscopy.

Tensile tests were performed with strain rate 0.001 s^{-1} for PS and $PS_{0.91}VBA_{0.09}$ at room temperature. Strain softening is observed in both samples, while the yield stress increases with hydrogen bonding content, and the slope after the yield point is almost the same. According to the Haward and Thackray model, [1] the hydrogen bonding contributes to the inter-molecular stress but not to the network stress. Besides, the Young's modulus is 4 GPa for both samples.

3-point bending tests were performed for all the samples to investigate the influence of hydrogen bonding on bending stability. The bending modulus is also around 4 GPa, which agrees with the Young's modulus from tensile tests. Besides, it is worth pointing out that the ductility of these anisotropic polystyrenes increases with hydrogen bonding content, since the strain related to maximum stress increases accordingly. The average values of strain at the corresponding maximum stress for PS, $PS_{0.95}VBA_{0.05}$ and $PS_{0.91}VBA_{0.09}$ are 5.31%, 6.35%, and 7.35%, respectively.

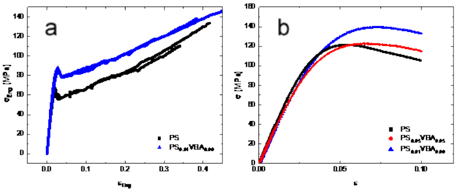

Fig.3 Mechanical testing results: a) tensile test, b) 3-point bending test

Conclusion

Linear viscoelastic measurements and non-linear extensional rheology confirm the absence of hydrogen bonding in the modified PS above T_g, which allows the processing of flexible, anisotropic polymer filaments. While in vitrified state, the formation of hydrogen bonding is confirmed by IR spectra. By introducing hydrogen bonding, the stretched and quenched filaments have increased yield stress and ductility.

Acknowledgements

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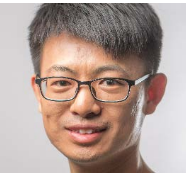
Particle deposition in high temperature processes

(April 2019- March 2022)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

The global energy consumption has increased during the past decades due to industrialization and urbanization. To reduce the energy consumption, an important measure is to increase the energy efficiency in energy demanding industry, such as cement and stone wool production processes. A high efficiency and stable operation of these processes is challenged by the formation of deposits, which reduces the heat transfer efficiency and causes unstable operation. It is therefore desirable to improve the understanding and develop countermeasures for particle deposition in industrial high temperature processes.



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Abstract

This PhD project aims to achieve an improved understanding and modelling capability of particle deposition in industrial high temperature processes, especially in cement and cyclone-based stone wool production processes. The influence of gas properties, particle properties, and operating conditions will be investigated in a pilot scale entrained flow reactor under conditions similar to cement and stone wool production processes. Based on the experimental results, an advanced chemical engineering model will be developed to predict deposit formation. Finally, the developed model will be validated in the simulation of full-scale cases coupling with CFD.

Introduction

Particle deposition occurs in many minerals based industrial high temperature processes, such as cyclone-based stone wool production process and cement production process. In these processes, it is often not the fuel ash but the mineral feed that mainly causes deposit formation, and the deposition typically occurs on refractory lined surfaces. In some cases, moderate deposition is wanted and helps to decrease heat loss. However, excessive deposition may lead to reduced heat transfer efficiency, blockage of flue gas channels, and sometimes even cause unscheduled plant outage[1,2].

Cement production can be generally divided into three consecutive process: (1) raw material preparation, (2) pyro-processing and (3) clinker processing. The pyro-processing process usually consists of cyclone preheaters, a calciner, a rotary kiln and a clinker cooling[3]. Particle deposit build-up tends to occur in the preheaters and rotary kiln. In a preheater tower, the raw materials are heated counter-currently by the high temperature flue gas from a calciner. The flue gas may contain a large amount of gas phase inorganic species that could condense on colder surfaces and particles. Subsequently, the condensation products may cause deposit buildup on the cyclone walls. It has been reported that the main constituents of the buildup samples are S, K and Ca and Cl, with the composition varying significantly at different locations[4]. In a rotary kiln with a high temperature around 1200-1400℃, coating or ring formation by clinker or dust may occur on the wall of the kiln. The formed coating in different locations may have different shape and thickness[3].

Stone wool is an insulation material widely used in buildings. During the production of stone wool, a mineral feed is melted in a cyclone combustion chamber at temperatures above 1400℃. In the cyclone combustor some both wanted and unwanted deposits may be formed by the mineral feed. A melt is formed on the cyclone wall that collects material, induce further melting of solid particles and lead the melted minerals towards the outlet. In colder parts of the cyclone combustion chamber non melted deposits may be formed, that can be difficult to remove and may interfere with plant operation.

Particle deposition in combustion systems using biomass and coal has been studied extensively through laboratory and pilot-scale experiments, full-scale measurements, and modelling[5]. However, particle deposition in mineral feed based industrial high temperature processes, which usually involves different temperature and gas atmosphere conditions, different surfaces, and deposition locations, has only been studied limitedly. An improved understanding and modelling capability of particle deposition in industrial high temperature processes is wanted.

Specific objectives

The specific objectives of this project are:

- To obtain an improved fundamental understanding of particle deposition processes in cement production and cyclone-based stone wool production process;
- To obtain a capacity to predict deposition behaviors of industrial raw materials including the influences of fluid dynamics, gas atmosphere, heat transfer and composition of mineral feeds;
- To illustrate that the developed particle model is applicable to describe the particle deposition in the industrial-size;

Methods

High temperature particles deposition will be studied in a pilot-scale entrained flow reactor (EFR) at DTU Chemical Engineering. As illustrated in Figure 1, the setup consists of a gas supply system, a particle feeding system, a gas preheater, a 2m long electrically heated reactor (inner diameter 8 mm) which can reach 1450℃, a deposition probe system, and a bottom chamber.

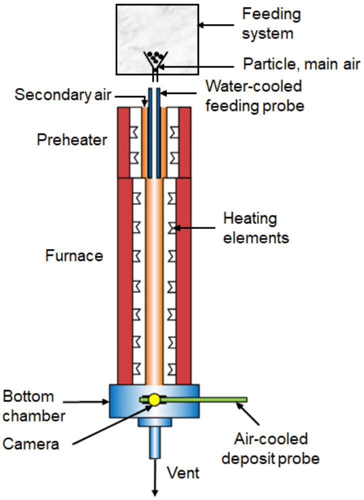

Figure 1. Schematic drawing of the pilot scale Entrained Flow Reactor[6]

The influence of particle properties (density, chemistry, viscosity), deposit probe properties (material, temperature) and operational conditions (furnace temperature, gas velocity, gas atmosphere, particle flux) will be investigated.

A chemical engineering model describing ash particle deposition process will be developed based on the experimental data. The model will consider the deposition mechanisms of condensation, inertial impaction, and thermophoresis.

Finally, the deposition model is expected to be coupled with CFD to simulate the particle deposition in cement and stone wool production processes.

Acknowledgement

This project is funded by China Scholarship Council (CSC), Technical University of Denmark (DTU), and the ProBu project funded by Innovation Fund Denmark and ROCKWOOL A/S, FLSmidth A/S and DTU.

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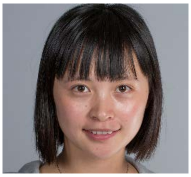
Catalytic Oxidation of Methane

(September 2016- August 2019)

Contribution to the UN Sustainable Development Goals

In order to mitigate the emissions of SO_X, NO_X, and particulates natural gas is a promising and environmentally friendly alternative to diesel fuel for ships in coastal zones. However, typical natural gas fired engines emit significant amounts of unburnt methane (CH_4) to the environment causing a severe greenhouse gas (GHG) effect. Therefore, efficient catalysts for full oxidation of the unburnt methane escaping from the engine are needed to enable the utilization of the cleaner fuel, natural gas, in the marine sector.



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Abstract
Natural gas is an interesting engine fuel for ships in coastal zones, where high sulfur marine fuels cannot be used. However, the unburnt methane from the engines poses another severe emission problem. The current study seeks to develop a catalyst for methane emission abatement from natural gas engines. Motivated by the good performance of the commercial Rh catalyst, zeolite supported Rh and Pd catalysts were prepared and tested for methane oxidation in the temperature range of 250-600 °C, in a simulated exhaust gas (2500 ppm CH_4, 10 vol.% O_2, 5 vol.% H_2O, and 1-20 ppm SO_2 when present). Compared with Pd catalysts, Rh supported on ZSM-5 catalysts shows comparable activity at the same loading (2 wt.%), but higher SO_2 tolerance. For Rh/ZSM-5 catalyst, 79 % conversion can be achieved by operating at 500 °C and in the presence of 1 ppm SO_2 and 5 vol.% H_2O.

Introduction

The international maritime organization (IMO) has adopted the regulation that the marine ships shall not use fuel with a sulfur content greater than 0.5 % (m/m) from the year 2020 in coastal areas. Liquefied natural gas (LNG), natural gas that has been cooled to liquid state at about -160 °C, is sulfur free and therefore attracting growing interest as a viable alternative in coastal zones. However, the unburnt CH_4, which has a greenhouse impact of 26-38 times larger than that of CO_2, becomes another environmental issue for the Natural gas fired engines [1]. In order to solve this problem, a CH_4 catalytic oxidation unit, which could fully convert the unburnt CH_4 to CO_2 and H_2O, is necessary in the after-treatment unit.

For lean-burn gas engines, the exhaust gas composition is summarized in Table 1 [2]. Besides CH_4 and excess O_2, a high concentration of H_2O and < 1ppm SO_2 (from LNG odorant and engine lubricating oil) are always present. The temperature that can be achieved in the exhaust gas system is at most 495-540 °C, if the catalyst can be placed before the turbine inlet. To offer a practically applicable solution a catalyst should thus be able to offer high conversion at a temperature of the order of 500 °C with as high a space velocity as possible to keep costs and equipment volume to a minimum.

Table 1. Exhaust conditions of gas engines [2].

Components	Content
CH_4	< 500-9000 ppm
O_2	~ 10 vol.%
H_2O	> 5-15 vol.%
CO_2	~ 3 vol.%
CO	500-1000 ppm
SOx	1 ppm
NOx	350-600 ppm

The catalysts for CH_4 oxidation can be divided into two groups, namely noble metal based catalysts (Pd, Pt, Rh, Au) and non-noble metal based catalysts [3]. Removal of CH_4 in the absence of H_2O or SO_2 can be achieved on noble metal catalysts, especially Pd/Al_2O_3 based catalysts with a mixture of PdO_x and Pd^0 as the most active phase. However, the activity of Pd/Al_2O_3 catalysts is strongly inhibited by the presence of H_2O or SO_2, and more detrimentally by the combined presence of H_2O and SO_2. A catalyst that can be operated under the exhaust gas condition, where both H_2O

and SO_2 are present, with no requirement for regeneration would be very attractive.

For CH_4 oxidation, Rh was reported to be initially less active than Pd but more SO_2 tolerant [4].

Specific objectives

The objectives of this PhD project focus on developing a catalyst which can be used under practical engine exhaust conditions: low temperature (< 550 ℃), 2000-2500 ppm CH_4, presence of of H_2O (~ 10 vol. %), and SO_2 (~ 1 ppm). The scope of the PhD work includes:

- Literature study.
- Activity, stability and SO_2 resistance tests of the commercial Rh catalyst.
- Catalyst preparation: Rh and Pd supported on zeolites, SiO_2, Al_2O_3.
- Thermal, water and SO_2 deactivation of the Rh catalysts at different temperatures (400-600 °C), SO_2 concentrations (1-20 ppm).
- Catalyst characterization: fresh and spent.
- Identification of the optimum operation conditions.

Results and discussions

As shown in Figure 1, the conversion of CH_4 over the commercial Rh catalyst could stabilize at 22 % after running in the presence 5 vol.% H_2O and 20 ppm SO_2 for 240 h. After removal of SO_2 from the inlet, the activity was restored to 45 % without extra heating (Figure 1).

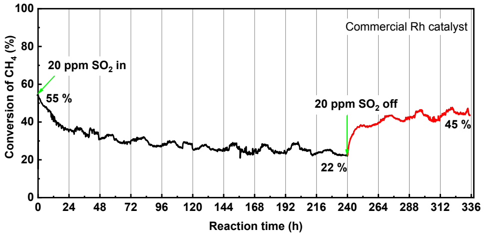

Figure 1: Conversion of CH_4 on the commercial Rh catalyst. Conditions: 2500 ppm CH_4, 10 vol.% O_2, 5 vol.% H_2O, 20 ppm SO_2, balanced with N_2. GHSV=75,000 Nml/(g_{cat}·h).

The performance of lab-prepared 2 wt.% Rh/ZSM-5 and 2 wt.% Pd/ZSM-5 catalysts are compared in Figure 2. Figure 2a shows that Rh is clearly superior to Pd under these conditions. Figure 2b illustrates that with 5 vol.% H_2O and 1 ppm SO_2, conditions characteristic of real exhaust gases, the Rh/ZSM-5 catalyst is able to achieve a high conversion of 79 % at 500 °C. This occurs at a relatively high space velocity corresponding to GHSV=7500 L/($g_{noble\ metal}$·h), which compares favorably to field tests with catalyst coated monoliths that typically apply space velocities in the range of 3500-7000 L/($g_{noble\ metal}$·h) [5]. The presently achieved performance with powdered catalysts should thus also indicate favourable performance of practical monolith systems.

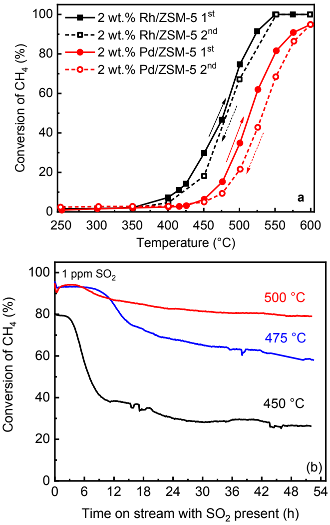

Figure 2: Conversion of CH_4 on 2 wt.% Rh/ZSM-5 and 2 wt.% Pd/ZSM-5 in the presence of 5 vol.% H_2O and 20 ppm SO_2. (b) Conversion of CH_4 on 2 wt.% Rh/ZSM-5 in the presence of 5 vol.% H_2O and 1 ppm SO_2 at 450, 475, and 500 °C. Conditions: 2500 ppm CH_4, 10 vol.% O_2, 5 vol.% H_2O, 1 or 20 ppm SO_2, in N_2. GHSV=150,000 Nml/(g_{cat}·h).

Conclusions

Rh/ZSM-5 is able to reach a high CH_4-conversion under simulated exhaust conditions – achieving 79 % conversion at 500 °C and GHSV=150,000 Nml/(g_{cat}·h) in the presence of 1 ppm SO_2 and 5 vol% H_2O. This ability to reach a high methane conversion at conditions achievable in a lean-burn engine exhaust system upstream the turbocharger offers promise that this catalyst could be a practically applicable solution to the CH_4 emission challenge from natural gas fired engines.

Acknowledgements

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Mechanisms of High Temperature Agglomeration in Fluidized Beds

(May 2018- May 2021)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

Biomass is a renewable energy resource and is considered as a substitute for fossil fuels. About 15% of current global energy supply is contributed by biomass, and it is estimated that up to 33–50% of the global primary energy consumption will be provided by biomass by 2050. Fluidized bed combustion and gasification are widely applied technologies for utilization of biomass. However, agglomeration strongly affects the operation of a fluidized bed and may lead to defluidization and unscheduled plant shutdown. Therefore, an improved understanding of agglomeration is important for an efficient utilization of biomass in fluidized bed reactors.

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Abstract

This PhD project focuses on understanding the mechanisms of high temperature agglomeration in fluidized bed combustion and gasification of biomass. The effect of gas atmosphere, bed temperature, biomass properties, and bed materials on agglomeration will be studied in a laboratory scale fluidized bed reactor under combustion and gasification conditions. Based on the experimental results, a model will be developed to evaluate the agglomeration tendency and countermeasures will be tested and optimized.

Introduction

Bed agglomeration in fluidized bed utilization of biomass at high temperatures is mainly attributed to the presence of a molten phase, i.e. a low melting point alkali containing compounds, which is originated from the interactions of the alkali species from biomass and bed materials (mainly SiO_2) [1]. However, the agglomeration tendencies and mechanisms during biomass combustion and gasification are still not fully understood. An improved understanding of agglomeration is wanted in order to develop effective countermeasures for bed agglomeration and defluidization.

Experimental

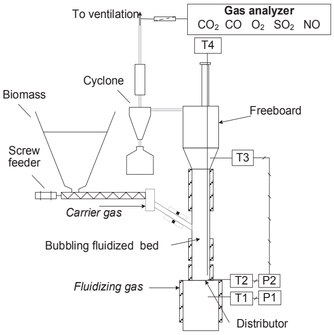

Figure 62: Schematic of a lab-scale fluidized bed reactor.

Table 8: Properties of wheat straw

Proximate analysis (wt.%, ar)	Moisture			**Ash**		
	8.5			**6.7**		
Ultimate analysis (wt.%, db)	C	H	N	O*	S	Cl
	42.8	6.1	0.8	42.9	0.1	0.1
Ash composition (wt.%, db)	Al	Ca	**K**	Mg	**Si**	P
	0.2	0.3	**1.0**	0.1	**1.1**	0.1

* Calculated by difference

Experiments were performed in a lab-scale fluidized bed reactor, as illustrated in Figure 1. Wheat straw (WS) with a size range of 2 - 4 mm and silica sand (SiO_2 > 97wt.%) with a size range of 355 – 500 μm were used as fuel and bed material, respectively. The proximate analysis of WS is shown in Table 1. 500 g of material (sand) was loaded in each experiment. During the experiments, the fluidizing gas was introduced at the bottom of the reactor. 100v.% Air, 25v.% steam/75v.% N_2, and 25v.% steam/2v.% O_2/73v.% N_2 were used as the fluidizing gas for the combustion, steam gasification and steam/air gasification process, respectively. The fuel was continuously fed into the reactor until defluidization point, which indicated by a sudden decrease or increase of the pressure drop, was observed. The corresponding feeding rate was around 0.110 kg/h, which is calculated according to an overall excess air ratio (λ) of 1.45 during combustion process. The bed temperature during all experiments was 850°C. The defluidization tendencies under three different atmospheres were evaluated by the amount of the injected fuel that caused defluidization.

Results

As shown in Figure 2, the amount of fuel needed to cause defluidization under three conditions increases in an order: steam/air gasification < combustion < steam gasification, implying that the agglomeration tendency decreases in an order: steam/air gasification > combustion > steam gasification.

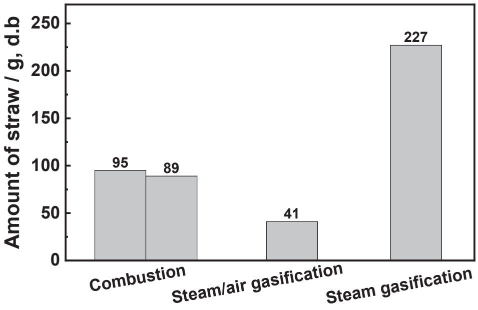

Figure 63: The amount of the injected fuel that caused defluidization under three conditions.

The bed samples taken from the reactor under three conditions are shown in Figure 3. The bed sample from steam gasification was much darker than other two conditions, which indicates a higher carbon amount in the bed.

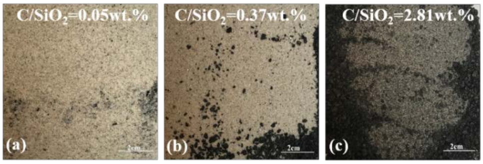

Figure 64: Bed samples taken from the cold reactor. (a) Combustion; (b) Steam/air gasification; (c) Steam gasification.

In order to investigate the impact of char during steam gasification, a stepwise gasification was performed. In the first step, around 50 g of straw was gasified under steam gasification condition. During the second step, the fluidizing gas was shifted to 100v.% N_2, 25v.% steam/75v.% N_2 or 25v.% air/75v.% N_2.

Table 9: Summary of stepwise gasification

No.	Fluidizing gas in 2nd step	Time (min)	Fuel (g)	Def.
1	100% N_2	36	47	No
2	25% steam/75% N_2	7	48	Yes
3	25% air/75% N_2	2	50	Yes

The results of stepwise gasification are summarized in Table 2. It is found that no defluidization was observed when 100v.% N_2 was used as fluidizing gas in the second step, while the defluidization occurred when the char was consumed by combustion or gasification in the second step. It indicates that char could inhibit the defluidization.

Discussion

The faster defluidization tendency during steam/air gasification than combustion may can be explained by the presence of high concentration steam and reducing atmospheres in the bed. KCl and K_2SO_4 are the typical K-species form during biomass gasification and combustion.[2] With the presence of high concentration of steam, K-silicates, which will melt at operating temperature, could be formed due to the interaction between KCl and SiO_2.[3] In addition, K_2SO_4 would transform into K-silicates under the reducing atmosphere formed during gasification process.[4] However, during steam gasification process, large amounts of char particles accumulate in the bed. The amount of molten phase, which is originated from the K-species in the biomass, in the bed could be greatly reduced because a significant amount of K-species remains in the char particles [5]. Moreover, the fine char particles attached on the sand surface, which made the sand much darker than other two conditions, may inhibit the interaction between ash and SiO_2. Therefore, presence of char particles maybe responsible for slower defluidization during steam gasification.

Conclusion

The composition of the fluidizing gas strongly affects the defluidization tendency during biomass utilization. The defluidization tendency decreases in an order: steam/air gasification > combustion > steam gasification. The high steam concentration and reducing atmosphere in the bed may be responsible for the faster defluidization during steam/air gasification than combustion. However, the presence of large amounts of char particles may lead to slower defluidization tendency during steam gasification.

Acknowledgement

This project is funded by China Scholarship Council (CSC) and Technical University of Denmark (DTU).

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A novel poly(vinyl chloride) gel used as soft electroactive material for sustainable energy harvesting

(May 2019 - April 2022)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

Plasticized PVC gel is a soft electroactive polymer offering large deformations under electric stimulation, due to its attractive features such as excellent flexibility and high response rate. It can either be used as actuator by applying on electric charge or used as energy generator based on the capacitive behavior. The unique performances enable plasticized PVC gels to become a promising material category for highly efficient and environmentally sustainable energy harvesting, which opens up the possibility to further exploit renewable and inexhaustible sustainable energy sources like water and wind.

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Abstract

Plasticized PVC gel is considered as a suitable material candidate for soft transducers, because of its excellent performances such as large strain, high output stress, and low driving voltage. In this study, transparent and electroactive plasticized PVC gels were prepared with varying plasticizer (dibutyl adipate, DBA) content. The prepared PVC gels were characterized using tensile analysis and dielectric spectroscopy. The results showed that the electromechanical properties of the plasticized PVC gels were affected by the DBA content. Both softness and dielectric permittivity were increased with increased DBA content, showing very promising for transducer applications.

Introduction

Polymers, due to the low fabrication cost, flexibility and light weight, are being studied intensively. In organic electronic materials, functional polymers have been widely studied as electroactive polymers (EAPs) in recent years [1-3]. EAP transducers can be typically classified into two types: ionic EAP transducers and electronic EAP transducers [1]. The competitive advantage of the ionic EAPs, e.g. conductive polymers (CP) [4] and ionic polymer-metal composites (IPMC) [5], is their low driving voltage (< 3 V). Nevertheless, this type of transducer may have limitations due to the relatively slow response and limited lifetime [6]. On the other hand, the electronic EAP type (e.g. dielectric elastomer transducers, DETs) is more promising for applications because of high strain, response speed and energy density [7]. However, conventional silicone-based DETs are facing the challenge of a high driving voltage of several kilovolts, which may hinder their commercial applications.

Poly(vinyl chloride) (PVC) is a highly commercial, low-priced material widely used in industry. With a certain amount of plasticizer added, the PVC becomes flexible and achieves an electrical response. The highly plasticized, flexible PVC is denoted PVC gel. The PVC gel can actuate due to the plasticizer migration which causes deformation under an electric filed. Additionally, the lone pair of electron from the chlorine atom in the PVC can strengthen the backbone of the polymer, thereby rendering appreciably good mechanical properties, and PVC displays excellent miscibility and compatibility with guest additives, which is advantageous for multi-functionalization of PVC gels.

Specific Objectives

This study will be conducted with the following objectives.

1. Synthesize PVC with different molecular weight to study the effect of molecular weight on the performance of PVC gel
2. Study the effect of plasticizer on the performance of PVC gel
3. Explore the mechanism(s) of electro-stimulated deformation of PVC gel
4. Select the appropriate additives for preparing multifunctional (e.g. self-healing, conductive) PVC composites
5. Assemble the PVC gel into transducer devices and test the performances

Results and Discussion

PVC gels were prepared with varying plasticizer content (PVC to DBA mass ratio, 1:4 and 1:8, denoted by DBA4 and DBA8). The results indicate that the amount of plasticizer plays an important role on the mechanical and dielectric characteristics of the PVC gels.

The stiffness of PVC gels decreases dramatically with increased DBA content (Figure 1 and Table 1). This is due to the liquid plasticizers departing from the main polymeric chain segments and thus making the gel softer.

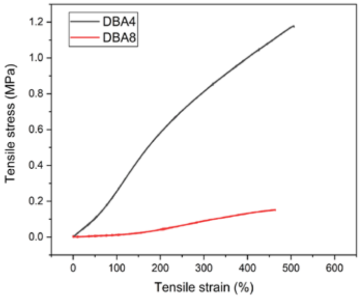

Figure 65: Stress-strain curves of the PVC gels with varying loadings of DBA at room temperature (RT).

Table 1: Mechincal properties of the PVC gels with varying loadings of DBA at RT.

Sample	Young's modulus (MPa)	Strain at break (%)	Tensile strength (MPa)
DBA4	0.24±0.02	491±13	1.13±0.05
DBA8	0.03±0.01	502±56	0.15±0.02

With the increased DBA content, the dielectric relative permittivity increases dramatically as seen in Figure 2. Due to the existence of C=O bond, the DBA has strong polarizability. As the amount of DBA increases, the number of dipolar movements increases, and the dielectric relative permittivity increases.

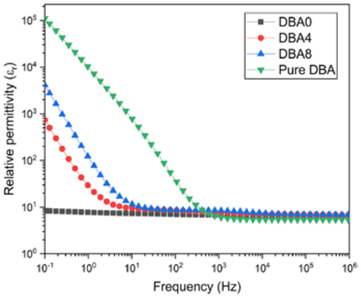

Figure 2: Relative permittivity ε_r of the PVC gels with varying loadings of DBA, and pure DBA at RT.

Conclusions

In this study, the mechanical and dielectric properties of PVC gels with varying PVC to DBA ratios (i.e. 1:4 and 1:8) were presented. When the content of DBA in PVC gel increased, the gel showed higher electromechanical performance. The proposed plasticized PVC gel holds promising applications of EAP transducers.

Acknowledgements

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Tubular Membrane Reactors for Immobilization of Enzymes

(March 2018 – February 2021)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

With the current global focus on minimizing the natural resources and toxic materials used, and the waste and pollutants generated in the entire production process, this project aims at finding alternative and more sustainable methods of synthesis by combination of polymers and enzymes. Particularly, this projects targets production of fine and specialty chemicals, such as active pharmaceutical ingredients. The project is focused on development of new tube-in-tube systems, spanning new membrane systems as well as gas-liquid phase reactions in continuous flow.

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Anders Daugaard, John Woodley, Manuel Pinelo

Abstract

Enzymatic reactions offer a greener alternative to conventional catalytic processes. A major challenge in reaction bioengineering is purification of the final product from the catalyst residues. Membrane bioreactor technology can serve as an efficient tool for enzymatic reactions and product purification at the same time. Good control over the separation properties is a crucial factor here for an efficient purification process. In our work, a combination of surface chemical modification and pore collapse was employed to tailor the retention of a solute in commercial hollow-fiber ultrafiltration membranes.

Introduction

Polyethersulfone (PES) membranes have been widely used in industrial applications due to their ease of production as well as thermal, chemical and mechanical endurance. PES membranes often find applications in ultrafiltration. By modification of the membranes, their solute retention can be tailored and their application range can be extended.

Surface-initiated atom transfer radical polymerization (SI-ATRP) is a versatile technique allowing the surface chemistry of PES membranes to be altered in a controlled manner by introducing various polymers with a wide selection of functional groups. To allow SI-ATRP to take place, the membrane must first be activated by introduction of an ATRP initiator. Heterogeneous ortholithiation has been reported for flat-sheet PES membranes by Guiver *et al.* [1], which was extended by our group with acylation of a range of acyl chlorides [2,3]. This opens up for post-modification of membranes by SI-ATRP.

Another process that has high impact on performance of PES membranes is pore collapse. Pore collapse is a well-known phenomenon resulting in loss of the porous microstructure upon drying. No studies have been found on how pore collapse affects the retention characteristics of membranes.

Specific Objectives

The objective of the project is preparation of surface functional tubular membrane modules with full control over separation properties. Ultimately, these systems will be applied as biocatalytic tubular membrane reactors (Figure 1).

Figure 66: Biocatalytic tubular membrane reactor – single-fiber module.

Results and Discussion

The impact of different surface chemistries on pore collapse and retention was investigated by preparation of a range of different polymer-grafted membranes. The original PES membrane was first activated by heterogeneous ortholithiation with n-butyllithium and subsequent acylation with 4-chloromethylbenzoylchloride to introduce benzyl chloride groups serving as initiators in the next step. Thereafter, SI-ATRP with 4 different monomers was performed to obtain polymer-grafted membranes, as shown in Figure 2.

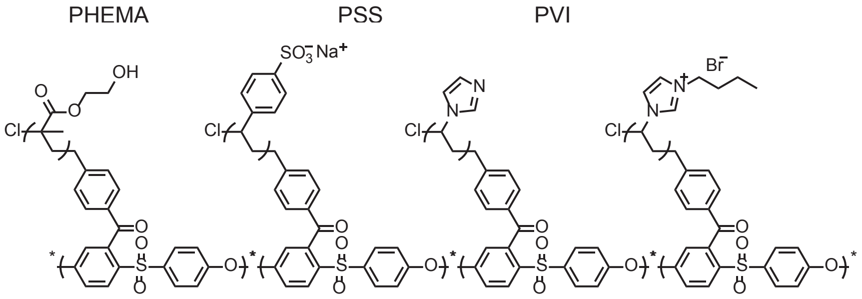

***Figure 67:** Different surface chemical modifications of polyethersulfone membrane.*

Before installing the membranes in the single-fiber modules (Figure 1), the modified membranes were either treated with glycerol to protect the pores, or else treated with ethanol to collapse the membrane by subsequent drying in air. The influence of the surface modifications and subsequent pore collapse on solute retention was studied. The effects on solute retention were exemplified using calcein (623 Da) as shown in Figure 3.

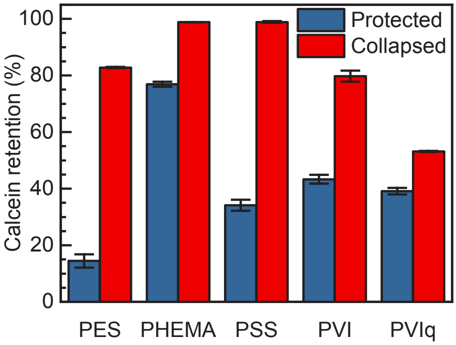

***Figure 68:** Calcein retention at 3 bar of pore-protected and pore-collapsed original PES, and modified PHEMA, PSS, PVI and PVIq membranes.*

As expected, calcein retention of the protected PES membrane is low (Figure 3). After the chemical modifications, the retention increases even in the glycerol-protected systems.

After allowing the pores to collapse, calcein retention of all the membranes is significantly higher as compared to their protected counterparts. PHEMA and PSS modified membranes reach almost full calcein retention due to extensive pore collapse shifting these membranes to a low-pressure nanofiltration mode. Retention in the mPVIq membranes does not increase as dramatically as in the other cases, since the pore collapse here is counterbalanced by the specific surface chemistry in the pores of the membrane.

Similarly, the different surface modifications also affect the water flux of the collapsed membranes and a balance between retention and flux will have to be found for a given system. For calcein the water flux of the collapsed membranes increases as PES < PHEMA < PSS < PVI < PVIq.

Conclusions

Commercial hollow-fiber ultrafiltration PES membranes were for the first time surface-modified via SI-ATRP. Membranes with a range of surface chemistries were prepared and tested in single-fiber membrane modules. The polymer grafting could be used to control the solute retention of the membranes. Selective membrane pore collapse could be exploited to obtain higher retention. The chemical nature of the grafted polymer is directly reflected in the retention and the extent of pore collapse.

We have here shown how intentional pore collapse can be used to achieve membranes with higher solute retention. This provides a platform for tailoring membrane properties to specific applications, which greatly extends the application range of ultrafiltration membranes and opens up for use of these membranes in biocatalytic tubular membrane reactors.

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